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SULFIDE PRECIPITATION OF NICKEL AND OTHER HEAVY METALS FROM SINGLE- AND MULTI-METAL SYSTEMS

by

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Precipitation behavior of heavy metals (Ni, Co, Cd, Cu, and Zn) was studied extensively in single-and multi-metal systems. Kinetic studies showed that NiS oxidation (as a function of pH, oxygen, and reaction time) caused the dissolution of NiS. CoS precipitation would require high pH, short detention times, or closed reactors (under N_2 atmosphere). In the multi-metal systems without nickel, CdS and ZnS precipitation were the same as in their single-metal systems; however, the precipitations were affected in nickel, CdS and ZnS precipitation were the same as in their single-metal systems; however, the precipitations were affected in nickel-containing systems because of NiS oxidation. Results of CdS precipitation from multi-metal systems (with or without nickel) were substantially better than the single-metal case.

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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxic Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmetnal problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This report describes work undertaken to evaluate the effectiveness of sulfide precipitation of nickel, cobalt, cadmium, copper, and zinc from single and multi-metal systems. The technical data obtained in this work can be used for the design of multi-metal precipitation (with and without chelating agent) processes over a broad pH range.

Requests for further information regarding this sulfide precipitation study should be directed to the Industrial Wastes and Toxics Technology Division, Water Engineering Research Laboratory, Cincinnati, Ohio.

Francis T. Mayo, Director
Water Engineering Research
Laboratory

ABSTRACT

Precipitation behavior of heavy metals (Ni, Co, Cd, Cu, and Zn) was studied extensively in single- and multi-metal systems. Kinetic studies showed that NiS oxidation (as a function of pH, oxygen, and reaction time) caused the dissolution of NiS. CoS precipitation behavior was similar to NiS. Effective NiS (or CoS) precipitation would require high pH, short detention times, or closed reactors (under N_2 atmosphere). In the multi-metal systems without nickel, CdS^2 and ZnS precipitation were the same as in their single-metal systems; however, the precipitations were affected in nickel-containing systems because of NiS oxidation. Results of CuS precipitation from multi-metal systems (with or without nickel) were substantially better than the single-metal case.

The use of ultrafiltration proved that the particle size of CdS was influenced by pH. A higher pH (greater than 8) favored the formation of colloidal precipitates. The settling characteristics of precipitate were improved significantly by the addition of coagulants (anionic polymer or calcium). The effectiveness of the polymer was controlled by polymer type, pH, and polymer concentration. Freshly prepared CaS slurries were quite successful in supplying both sulfide source and coagulant.

This report was submitted in fulfillment of Cooperative Agreement No. CR-807760 by the University of Kentucky under the sponsorship of the U. S. Environmental Protection Agency.

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SECTION I

INTRODUCTION

Sulfide precipitation is a well known means of removing heavy metals from solutions because of the low solubilities of metal sulfides. A number of investigations have proved that sulfide precipitation processes are more effective in removing heavy metals from industrial wastewaters than the conventional hydroxide precipitation processes (1-10). Industrial wastewaters usually contain a mixture of heavy metals; however, most of the fundamental studies of sulfide precipitation were conducted using single-metal solutions. The interactions between different metals may have significant effects on the metal precipitation behavior. Most of the heavy metals, such as Cu, Cd, Zn, and Hg can be effectively precipitated at short contact times but for metals like Ni and Co, the precipitation kinetics is more complex because the post dissolution of nickel sulfide and cobalt sulfide.

At a pH < 10.0, dissolution of nickel sulfide occurs with time in open reactor systems (in the presence of oxygen). No dissolution has been observed in closed reactor systems. Several literature articles (3-4, 11-12) reported the observation of this phenomenon. The knowledge

of the mechanism of nickel sulfide reactions would be beneficial in terms of reactor design for multi-metal systems. Nickel ions have been reported to possess strong catalytic effects on sulfide oxidation (13). Mixed metal solution systems containing nickel are of particular interest because the presence of nickel may result in a stronger and more complicated metal interactions than would the presence of other metals.

Cobalt resembles nickel in many aspects and is a valuable strategic metal. A great deal of interest has been shown in its separation and recovery. Experimental data are needed to examine the effectiveness of cobalt removal by sulfide precipitation and to compare its precipitation behavior with that of nickel.

In the presence of chelating agents, selective separation of heavy metals may be possible because of the difference in stability among the various metal-chelate complexes. EDTA (ethylenediamine tetraacetic acid), a rather strong chelating agent, could be used in mixed metal solution systems to evaluate the effectiveness of this technique on metal separation with sulfide precipitation.

Metal sulfide precipitation tends to form colloidal precipitates which cause some separation problems in either settling or filtration processes. In order to meet increasingly stringent effluent standards for heavy metals,

several different approaches were considered to solve these problems. The addition of coagulants, such as polymer, can aggregate colloidal precipitates after sulfide precipitation. This may be an effective method to help separate the precipitates from solution. The addition of calcium sulfide slurry instead of sodium sulfide solution, to supply both a sulfide source and a coagulant [(CaII)] at the same time, may also be an effective technique.

SECTION 2
LITERATURE REVIEW

Most heavy metals encountered in industrial wastewaters form very stable metal sulfide precipitates. According to the type of sulfide source, several sulfide precipitation processes have been developed to remove heavy metals from wastewaters. Sulfide compounds, such as Na_2S, NaHS, H_2S, FeS, and CaS, have been used as sulfide sources in conducting sulfide precipitations.

Bhattacharyya et al.(1) evaluated a bench-scale study to establish the effectiveness of sulfide precipitation (for copper smelting wastewater) by the addition of sodium sulfide solution. The results showed a high degree of removal of As, Cd, Cu, Zn, and Se. Their further studies (3) on both bench-scale and full-scale systems demonstrated that a combination of hydroxide-sulfide precipitation was necessary to obtain satisfactory removal of arsenic, heavy metals and fluoride from a copper-lead smelter wastewater.

Sulfex, a patented sulfide precipitation process, uses a freshly prepared ferrous sulfide slurry, to precipitate heavy metals from metal finishing wastewaters. Scott (14) reported the application of this process (funded by EPA) at a full-scale plant for heavy metal

removal. Satisfactory removal of metals such as Cd, Cu, As, and Cr was achieved with residual concentrations lower than 0.05 mg/l.

Recently, Kim (15) developed a sulfide precipitation process using calcium sulfide slurries, prepared by reacting lime with hydrogen sulfide or sodium hydrosulfide, as sulfide sources. The bench-scale experiments showed effective removal of heavy metals (such as Cd, Cu, Pb, Ag, and Zn). He obtained residual metal concentrations below 0.05 mg/l in the absence of chelating plating agents.

Chelating agents, used widely as plating additives, have been found in wastewater streams at significant concentrations. In the presence of a chelating agent, hydroxide precipitation is not adequate to obtain satisfactory removal of some heavy metals (1). Helz and Horzempa (10) indicated that EDTA acted as a kinetic inhibitor and could block copper sulfide precipitation. Extensive studies of the effects of various chelating agents (such as EDTA, oxalate, tartrate, etc.) on sulfide precipitation were conducted by Ku (12). With high concentrations of strong chelating agents (such as EDTA), a substantial reduction in the extent of sulfide precipitation was observed for metal sulfides of high solubilities (such as zinc sulfide and nickel sulfide). For sparingly soluble metal sulfides, such as cadmium sulfide and copper sulfide, the chelating agent effects were insignificant.

Nickel behavior with sulfide precipitation is more complicated than other metals because of nickel sulfide dissolution. The primary nickel sulfide precipitate, so-called α-NiS, formed in aqueous solution is amorphous and is thermodynamically unstable (16). In the presence of oxygen, α-NiS tends to oxidize and generate other sulfur species such as NiS_2, Ni_3S_4, SO_4^{2-}, etc. Nickel sulfide dissolution was reported to be a strong function of reaction time in an open reactor system (at pH < 10) (4). Krebs (17) studied the effects of metal ions, such as Mn^{2+}, Ni^{2+}, Fe^{2+}, Co^{2+} ,and Cu^{2+}, on the rates of oxygen uptake in Na_2S, $(NH_4)_2S$ and H_2S solutions and found significant catalytic influences. In 0.5 M Na_2S and H_2S solutions, the catalytic effects followed the sequence : $Mn^{2+} > Co^{2+} > Ni^{2+} > Fe^{2+} > Cu^{2+}$. Chen and Morris (13) also found similar effects of the above metal ions on sulfide oxidation.

Karakulova and Luganov (18), demonstrated the equilibria of a Ni-S-H_2O system by thermodynamic analysis. Calculations from redox potential of all possible sulfur species yielded a schematic potential-pH diagram for the Ni-S-H_2O system. Because of the absence of thermodynamic data for $Ni(HS)_2$ and Ni(OH)(HS), the calculations did not involve these compounds.

Arai et al. (19) examined the oxidative leaching reaction of nickel sulfide in nitric acid from both thermodynamic and kinetic points of view. A schematic

potential-pH diagram for a Ni-S-H_2O system (at pH < 4.0) showed that the possible solid substances in the system were Ni, NiS, $Ni_{1-a}S$ and S^o. The main reaction of nickel sulfide in nitric acid was proposed:

$$3\ Ni_{1-a}S_{(s)} + 2(4-a)\ HNO_{3(aq)} + 3(1-2a)\ H^+_{(aq)} \rightleftharpoons 3(1-a)\ Ni^{2+}_{(aq)} + 3\ HSO^-_{4(aq)} + 2(4-a)\ NO_{(g)} + 4(1-a)H_2O \quad (1)$$

and the side reaction was:

$$3\ Ni_{1-a}S_{(s)} + 2(1-a)\ HNO_{3(aq)} + 6(1-a)\ H^+_{(aq)} \rightleftharpoons 3(1-a)\ Ni^{2+}_{(aq)} + 2(1-a)\ NO_{(g)} + 3S^o_{(s)} + 4(1-a)H_2O \quad (2)$$

The kinetic studies proposed a rate equation for overall reaction of the oxidative leaching of nickel sulfides:

$$-d[NiS]/dt = kA_{NiS} \cdot [HNO_3] \quad (3)$$

where k is a reaction constant, and A is the surface area of NiS particles.

SECTION 3

OBJECTIVES OF THIS INVESTIGATION

The overall objective of this investigation was to establish the kinetics and the extent of sulfide precipitation of selected heavy metals. The flocculation and coagulation of fine metal sulfide precipitates were also investigated. Extensive bench-scale experiments were conducted with both single metal and multi-metal solution systems.

The specific objectives included:

1. Establish the effects of pH, reaction time, initial metal concentration, sulfide dosage, and the presence of interfering ions on metal sulfide precipitation.
2. Study the kinetics of nickel sulfide dissolution.
3. Establish the metal interaction effects on metal precipitation behavior in selected multi-metal systems.
4. Apply metal-chelating agent complexation reaction for selective metal separation.
5. Improve the separation of fine metal sulfide precipitates by the addition of coagulants such as polymer and calcium ion.
6. Compare metal sulfide precipitation by Na_2S, freshly prepared CaS, and commerically available CaS.

SECTION 4

PRECIPITATION REACTION MODELS

GENERAL

The comparison of Ksp values of metal sulfide and the corresponding metal hydroxide is shown in Table 1. The differences in Ksp values reveal that the sulfide precipitation processes may have the greater potential to comply with the increasingly stringent effluent standards of heavy metal as compared with conventional hydroxide precipitation processes. Although the sulfide precipitation process overcomes the limitations of hydroxide precipitation, the sulfide precipitation process itself also has some limitations. For some metals, such as Ag, Sn, and Hg, the metal sulfides (Ag_2S, HgS, and SnS_2) may form soluble sulfide complex species (such as HgS_2^-, AgS^{2-}, etc.) with an excess of sulfide ions, thus increasing the solubilities. In the case of arsenic, the removal of As(III) can be achieved only at lower pH (pH < 4), and the removal of As(V) is not feasible by sulfide precipitation (11). With chromium, the reduction of Cr(VI) is possible only when Fe(II) is used as a coagulant in conjunction with sulfide (22).

In addition to the precipitation problems, the separation of metal sulfide precipitates from solutions is also considered a problem because of the formation of a great portion of fine or colloidal particle precipitates.

TABLE 1

Comparison of Solubility Product Constants

Metal ions	Log Ksp of Metal Sulfide(20)	Log Ksp of Metal Hydroxide(21)
Ag^{+}	- 49.7	- 7.7
Cd^{2+}	- 27.7	- 14.4
Co^{2+}	- 20.0	------
Cu^{+}	- 48.0	------
Cu^{2+}	- 35.1	- 20.4
Fe^{2+}	- 17.3	- 15.2
Hg^{2+}	- 52.4	- 52.4
Ni^{2+}	- 20.7	- 17.2
Pb^{2+}	- 27.0	- 15.3
Zn^{2+}	- 23.8	- 16.7

H_2S-HS^--S^{2-} EQUILIBRIUM

Sulfide compounds such as Na_2S, NaHS, and CaS, can be added as sulfide sources. When these compounds dissolve in water, $H_2S_{(aq)}$, HS^- and S^{2-} species are present. The following reactions express the relationship of these species:

$$H_2S_{(aq)} \rightleftharpoons H^+ + HS^- \qquad K_1=1.0\times10^{-7} \qquad (4)$$

$$HS^- \rightleftharpoons H^+ + S^{2-} \qquad K_2=1.2\times10^{-13} \qquad (5)$$

According to the equilibrium constants (K_1 and K_2), the distribution of the sulfur species was calculated (11) and is shown in Figure 1. At pH < 5, the predominant species is $H_2S_{(aq)}$, thus part of the $H_2S_{(aq)}$ may be lost to the air due to the $H_2S_{(aq)}$-$H_2S_{(g)}$ equilibrium (the $H_2S_{(g)}$ solubility is about 0.1 M in water at 25°C (23)).

METAL-LIGAND COMPLEXATION REACTION

A ligand may be an organic or inorganic anionic or neutral molecule. Ligands bind with the central metal ion to form a complex in a complexation reaction. In basic media, complexation of metal ions with hydroxide ions occurs as follows:

$$M^{2+} + n\ OH^- \rightleftharpoons M(OH)_n^{2-n} \qquad (6)$$

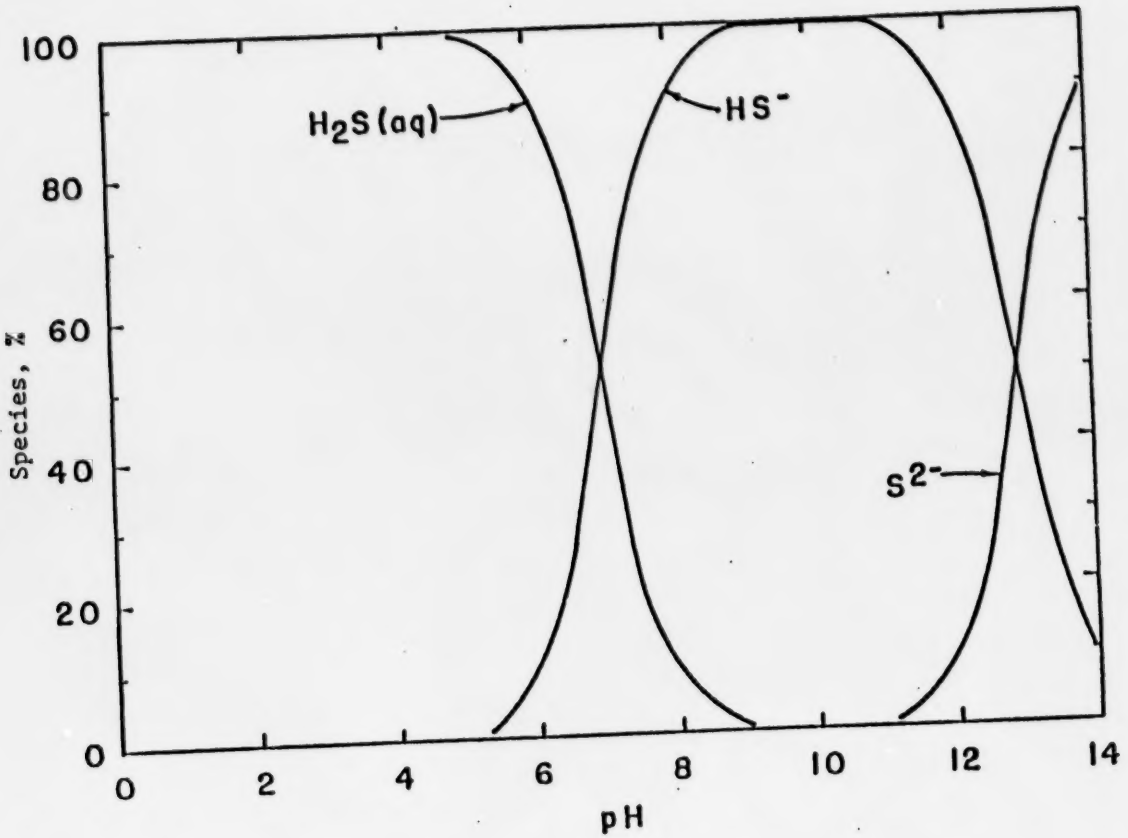

Figure 1. H_2S-HS^--S^{2-} Equilibrium.

A chelating agent which contains more than one pair of electrons is called a multi-dentate ligand. In the presence of chelating agents, additional complexation reactions have to be taken into account. The major complexation reaction (for example, with EDTA) forms a 1:1 type of complex with the divalent metal ion:

$$M^{2+} + L^{4-} \rightleftharpoons ML^{2-} \qquad K_{ML}=[ML]/[M][L] \qquad (7)$$

where L represents the ligand EDTA. Other side reactions are the stepwise protonation of the ligand:

$$L^{4-} + n\ H^{+} \rightleftharpoons H_nL^{n-4} \qquad (8)$$

and the formation of the protonated and the mixed-ligand complex species:

$$ML^{2-} + H^{+} \rightleftharpoons MHL^{-} \qquad (9)$$

$$ML^{2-} + OH^{-} \rightleftharpoons M(OH)L^{3-} \qquad (10)$$

where MHL is the protonated complex and $M(OH)L^{3-}$ is the hydroxy metal complex, so-called mixed-ligand complex.

These side reactions result in a reduction of the free ligand and the free metal ions. Thus the concept of an apparent stability constant, known as the conditional stability constant, has been introduced. The general form

of the overall conditional stability constant for a complex ML^{2-} is

$$K'_{ML} = [ML]/[M'][L'] \qquad (11)$$

where [M'] is the apparent free metal concentration, i.e. the concentration of metal ion that has not reacted with the chelating agent. [L'] is the apparent ligand concentration, i.e. the concentration of ligand not bound to the metal ion. Thus

$$[M'] = [M^{2+}] + [M(OH)^{+}] + \ldots + [M(OH)_n^{2-n}] \qquad (12)$$

$$[L'] = [L^{4-}] + [HL^{3-}] + \ldots + [H_nL^{-}] \qquad (13)$$

In order to find the relationship between the apparent and real free metal ion concentration, a quantity α_M, the so-called side-reaction coefficient of M, is defined as:

$$\alpha_M = [M']/[M] \qquad (14)$$

similarly

$$\alpha_L = [L']/[L] \qquad (15)$$

Therefore, equation 11 becomes

$$K'_{ML} = [ML]/[M][L] \cdot \alpha_M\alpha_L = K_{ML}/\alpha_M\alpha_L \qquad (16)$$

If the apparent concentration of all the complex species is of interest:

$$K'_{ML'} = [ML']/[M'][L'] \quad (17)$$

where

$$[ML'] = [ML] + [MHL] + [M(OH)L] \quad (18)$$

and

$$\alpha_{ML} = [ML']/[ML] \quad (19)$$

thus

$$K'_{ML'} = \alpha_{ML}/\alpha_M\alpha_L \cdot [ML]/[M][L] = \alpha_{ML}/\alpha_M\alpha_L \cdot K_{ML} \quad (20)$$

Figure 2 shows the relationship between $K'_{ML'}$ and pH for various metal-EDTA complexes.

METAL-SULFIDE REACTION

The primary reaction between a metal ion and a sulfide ion is to form a metal sulfide precipitate. For divalent metal ions (M^{2+}), the general reaction expression is:

$$M^{2+} + S^{2-} \; \underset{<---}{\overset{--->}{}} \; MS_{(s)} \quad (21)$$

With arsenite (As(III)), the reaction is expressed as:

$$2\ HAsO_2 + 3\ S^{2-} + 2\ H_2O \; \underset{<---}{\overset{--->}{}} \; As_2S_{3(s)} + 6\ OH^- \quad (22)$$

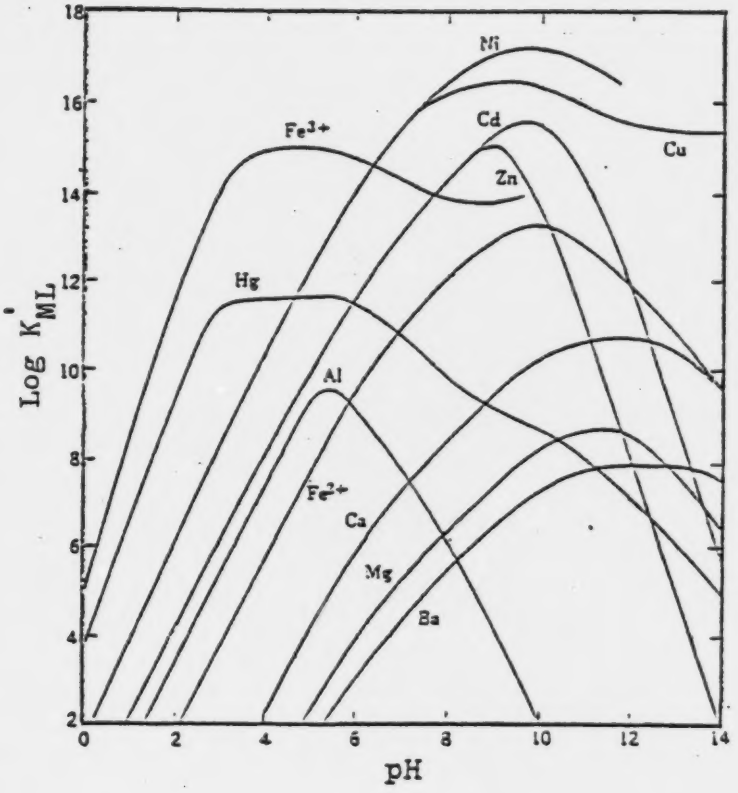

Figure 2. Apparent Stability Constants of Various M-EDTA Complexes as a Function of pH.

Since at higher pH the predominant hydroxide ions (OH^-) will force the reaction to the left, the precipitation of As(III) can only be achieved at the lower pH range. With metals such as Hg^{2+}, Sn^{4+}, and Ag^+, the metal sulfides are HgS, SnS_2, and Ag_2S, respectively. In the excess of sulfide ions, the complexation reactions may generate some soluble sulfide complex species, thus the soluble metal concentrations may increase. These reactions can be expressed by:

$$HgS + S^{2-} \rightleftharpoons HgS_2^{2-} \quad (23)$$

$$SnS_2 + S^{2-} \rightleftharpoons SnS_3^{2-} \quad (24)$$

$$Ag + S^{2-} \rightleftharpoons AgS^{2-} \quad (25)$$

$$Ag^+ + SH^- \rightleftharpoons AgSH \quad (26)$$

The sulfide precipitation of copper may involve the formation of CuS and Cu_2S:

$$Cu^{2+} + S^{2-} \rightleftharpoons CuS_{(s)} \quad (27)$$

$$2\ Cu^{2+} + S^{2-} \rightleftharpoons 2\ Cu^+ + S^o \quad (28)$$

$$2\ Cu^+ + S^{2-} \rightleftharpoons Cu_2S_{(s)} \quad (29)$$

In the case of cobalt and nickel, metal sulfides obtained by precipitation from aqueous solutions are primary α-forms which are thermodynamically unstable (16). The α-form metal sulfide, amorphous to X-rays, has the composition $M(SH, OH)_2$ where the content of OH^- depends on the pH value. In the presence of air, the precipitates are oxidized to generate MS_2, products containing hydroxide, SO_4^{2-}, etc. These reactions can be expressed by:

$$\begin{array}{ccccc} & & \gamma\text{-NiS}_{(s)} & & \\ & & \uparrow\downarrow \text{ low pH} & & \\ Ni^{2+} + S^{2-} & \rightleftharpoons & \alpha\text{-NiS}_{(s)} & \rightleftharpoons & \beta\text{-NiS}_{(s)} \\ & & \uparrow\downarrow O_2 & & \\ & & NiS_2 + SO_4^{2-} + \ldots & & \end{array} \qquad (30)$$

Bhattacharyya et al. (4) reported that the NiS dissolution with time is enhanced in the presence of oxygen. Karakulova and Lunganov (18) demonstrated the equilibria of the Ni-S-H_2O system by potential-pH diagram (Figure 3). The presence of several sulfur species (such as NiS, NiS_2, Ni_3S_2, S^o, SO_4^{2-}, $Ni(OH)_2$, Ni_3O_4, etc.) are possible.

EQUILIBRIUM REACTION CALCULATION

The overall considerations of H_2S-HS^--S^{2-} equilibrium, metal-ligand complexation and metal-sulfide

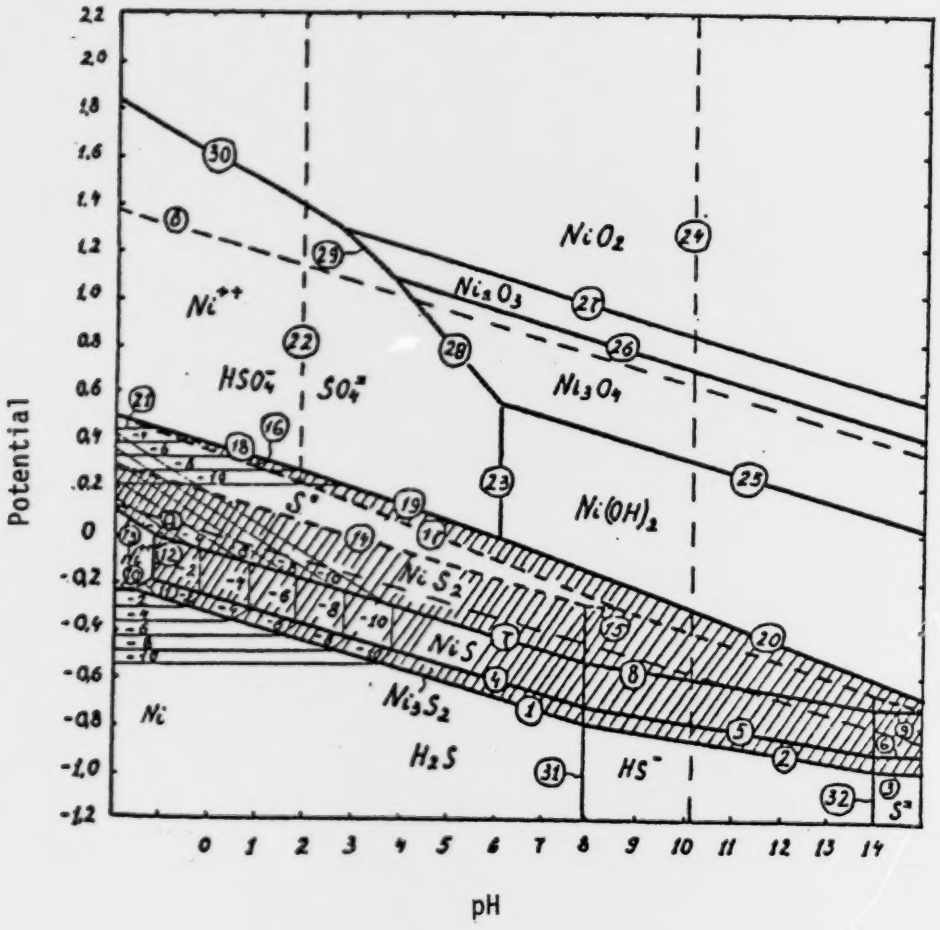

Figure 3. Potential-pH Diagram of Ni-S-H_2O System.

reaction are necessary to calculate the solubilities of metal as a function of pH, equilibrium soluble sulfide concentration S_T (the summation of $H_2S_{(aq)}$, $HS^-_{(aq)}$ and $S^{2-}_{(aq)}$), or chelating agent (EDTA) concentration.

Figure 4 shows the apparent metal concentration of ZnS, CuS, and NiS as a function of pH for different S_T. The apparent metal concentration is the total of all soluble metal species including M^{2+} and hydroxide complexes $M(OH)_n^{n-2}$. In this figure, the NiS oxidation is not taken into consideration. Thus the NiS solubility curves apply only to oxygen-free systems. The extent of precipitation decreases in the order CuS > CdS > ZnS > NiS because of the solubility products (Ksp) of metal sulfides. Typical literature value of metal sulfide solubility refers to the one at saturated S_T value. Compared with the metal hydroxide case, the solubilities of various metal sulfides are calculated and shown in Figure 5 as a function of pH. The solubility of metal sulfide is considerably lower and the precipitation is effective over a broader pH range than the corresponding metal hydroxide.

In the presence of EDTA, the solubilities of various metal sulfides were calculated (12) and are shown in Figure 6 as compared with the corresponding metal hydroxide. The extent of sulfide precipitation is still greater than that of hydroxide precipitation.

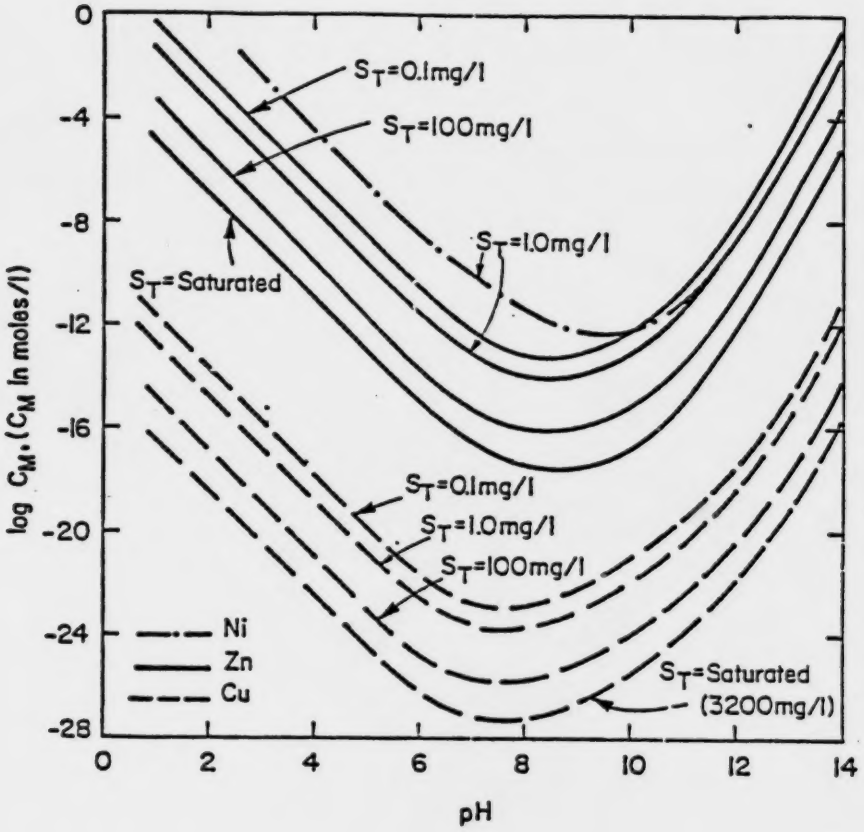

Figure 4. Calculated Solubilities of ZnS, CuS, and NiS as a Function of pH at Fixed Equilibrium Soluble Sulfide (S_T) Concentration.

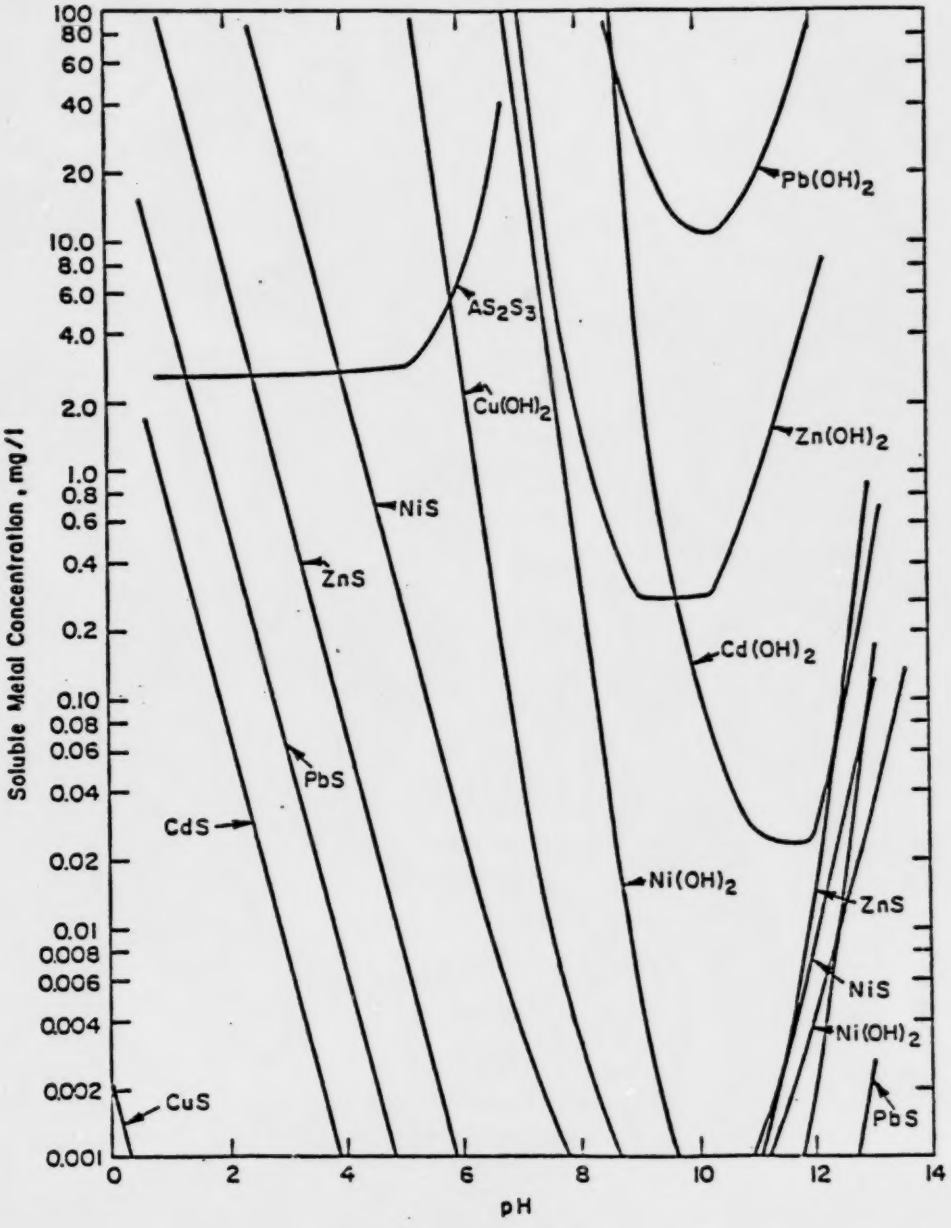

Figure 5. Comparison of the Solubilities Between Metal Sulfides and Hydroxides at Various pHs.

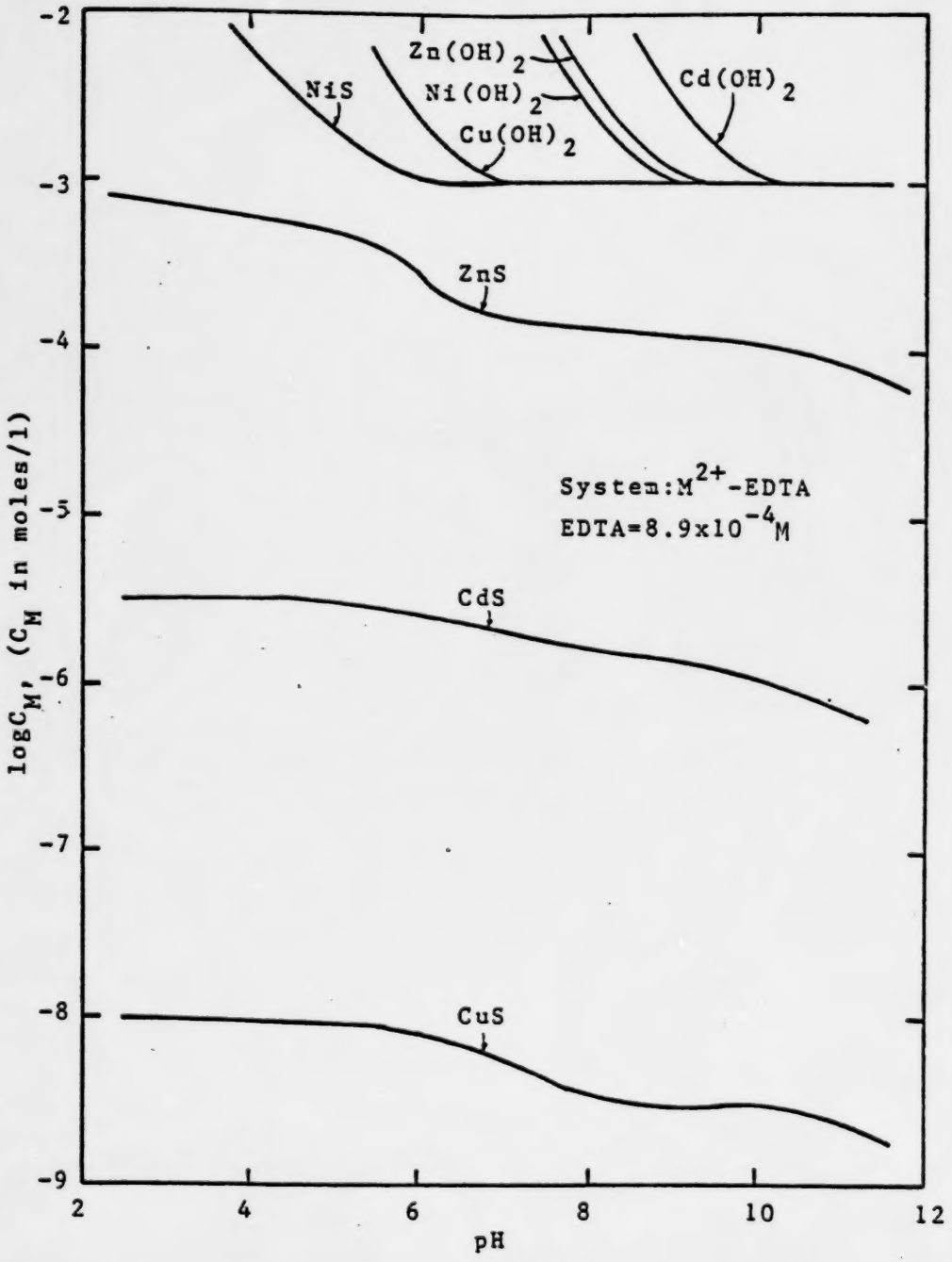

Figure 6. Comparison of Metal Sulfide and Hydroxide Solubilities as a Function of pH in the Presence of EDTA.

METAL SULFIDE PRECIPITATE PARTICLE GROWTH

Metal sulfide precipitation usually forms a large portion of fine or colloidal particle precipitates, especially for the metal sulfides with low Ksp values. In general, particle size is a function of pH, temperature, mixing speed, concentration of surrounding electrolyte and the reaction time (aging time). Thus, previous research on the precipitation of zinc sulfide from solutions have reported that the size of precipitate varied from 2 μm to 200 μm (26).

The pH affects the crystallite and aggregate size mainly because of the effect of pH on solubility and the extent of precipitation. A high degree of supersaturation causes nucleation to predominate over crystal growth, thus numerous small particles form at the beginning of the reaction. Zinc sulfide precipitation in alkaline media form smaller particles and the range of size appears to be larger compared to the acidic medium case.

SECTION 5

EXPERIMENTAL METHODS

GENERAL

In this study, most of the experiments were conducted with the addition of sodium sulfide solution into metal solutions. In some experiments, calcium sulfide slurry was used as a sulfide source. Two categories of metal solution systems, single metal and multi-metal, were used in either an open or a closed reactor at a controlled pH value. Polymers, used as coagulants, were added after sulfide precipitation in the sedimentation studies.

EQUIPMENT

Reactor and Accessory

Figure 7 shows the diagram of the apparatus. It included a reactor, pH control device, sodium sulfide injection and a mixer. Two types of reactors (open or closed) were used in this study. The open reactor was a one liter beaker and the closed reactor was a one liter five-neck round bottom flask. With the closed reactor, nitrogen gas was always supplied to maintain the pressure inside the reactor slightly above atmospheric pressure. The pH control device included a pH electrode, pH controller, and acid and alkali injection. For all the

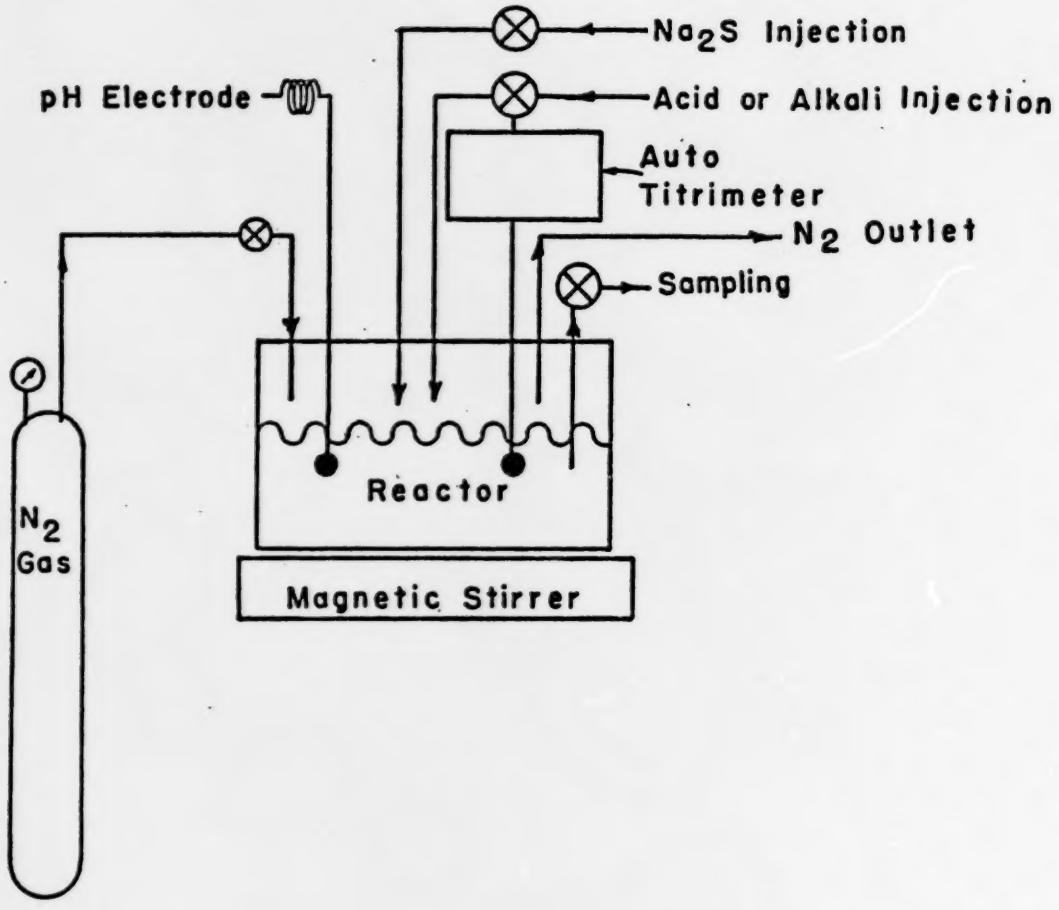

Figure 7. Schematic Diagram of Reactor System.

precipitation experiments, the reaction pH was controlled at a desired pH level within ±0.05 variation. A magnetic stirrer was used to generate high mixing speed to ensure complete mixing.

Filter

A Millipore filtration device with vacuum pump was used to separate the precipitate from solution. Filter paper with 0.45 μm pore size was chosen for most experiments. In some cases, an ultrafiltration membrane (10,000 MW cut-off) was used at 2 atm pressure.

Analyzer

A Varian AA-575 model Atomic Absorption Spectrophotometer was used to analyze heavy metals. The analytical accuracy was 1-5%. Table 2 lists the principal wavelength and sensitivity for the metal being studied.

CHEMICALS USED

The following analytical reagent grade chemicals were used in this study :

Aluminum sulfate	$Al_2(SO_4)_3.18H_2O$
Cadmium nitrate	$Cd(NO_3)_2.4H_2O$

TABLE 2

Sensitivity of Metals Obtained with Varian Atomic Absorption Spectrophotometer AA-575

Metal Ion	Wavelength (nm)	Sensitivity (mg/l)
Cd^{2+}	228.8	0.01
Co^{2+}	240.7	0.08
Cu^{2+}	324.8	0.04
Ni^{2+}	232.0	0.08
Zn^{2+}	213.9	0.01

Calcium chloride	$CaCl_2 \cdot 2H_2O$
Calcium sulfide	CaS
Cobalt chloride	$CoCl_2 \cdot 6H_2O$
Cupric nitrate	$Cu(NO_3)_2 \cdot 3H_2O$
EDTA disodium salt	$Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O$
Iodine	I
Nickel nitrate	$Ni(NO_3)_2 \cdot 6H_2O$
Nitric acid	HNO_3
Sodium chloride	$NaCl$
Sodium hydroxide	$NaOH$
Sodium sulfide	Na_2S
Sodium sulfite	Na_2SO_3
Sodium thiosulfate	$Na_2S_2O_3 \cdot 5H_2O$
Zinc nitrate	$Zn(NO_3)_2 \cdot 6H_2O$

Three types of polymer were used as flocculants in the settling experiments:

1. Cationic polymer : Nalcolyte 7129
2. Anionic polymer : Nalclear 7766
3. Nonionic polymer : Nalcolyte 7181

PROCEDURE

Preparation of Solutions

Metal solution

A known amount of metal nitrate salt was dissolved in double distilled water to prepare the stock solution. The metal solution concentrations varied from 50 to 5000 mg/l.

Sulfide solution

A known amount of sodium sulfide was dissolved in deoxygenized double distilled water to prepare the sulfide stock solution. The sulfide solution concentrations varied from 0.2 to 1.0 M. The stock solution was standardized iodometrically and stored in an amber bottle. Solutions of concentration less than 1.0 M were prepared daily.

Polymer solution

A known amount of polymer was dissolved in double distilled water and mixed at high speed for at least 30 minutes. Solutions of concentration less than 1% were used in 24 hours.

Experimental Procedure

Precipitation

A diagram of the apparatus is shown in Figure 7. The majority of the experiments were carried out in a beaker type reactor. The reactor and procedure were modified in order to study the effect of the concentration of dissolved oxygen. Metal solution of known concentration was transfered to the reactor. A magnetic stirring device was used to obtain high speed mixing. An automatic pH control unit including pH electrode, titrimeter, and pH controller was installed to maintain the pH of the reaction at the desired level. The reaction was started by adding a calculated amount of sulfide solution into the reactor. Samples were taken at various times and filtered immediately. The soluble metal in the filtrate was analyzed by an atomic absorption spectrophotometer.

Flocculation and settling

A known amount of polymer solution was added to the flocculating solution (obtained by using the above precipitation procedure). After mixing at 200 rpm for 5 minutes, the solution was transferred into a graduated cylinder 35 cm in height and 4.5 cm in diameter. A stirring device with constant speed control was installed in the middle of the cylinder. Further mixing was done at 100 rpm for 24 minutes and then at 200 rpm for one minute.

Samples were taken from the supernatant using a capillary pipette (at 2 cm below solution surface) at various times during settling. A few drops of concentrated nitric acid were added to the samples to dissolve the metal sulfide precipitate. These samples were then analyzed by an atomic absorption spectrophotometer.

SECTION 6

RESULTS AND DISCUSSION

The extent of metal sulfide precipitation is expected to be a function of pH, reaction time, initial metal concentration, sulfide dosage, and the presence of chelating agents and other interfering ions. With some metals, such as nickel and cobalt, the precipitation is dependent upon reactor system (closed or open).

Several different types of sulfide compounds (such as Na_2S, NaHS, $H_2S_{(g)}$, and CaS) can be used in metal precipitation. In this study, most of the experiments were conducted with sodium sulfide solution. Calcium sulfide was used in some specific experiments. Generally, experiments were conducted in open reactor system with a high mixing speed.

The separation results are reported in terms of residual metal concentration which refers to the amount of soluble (filtered through 0.45 μm filter) unreacted metal in solution. In some cases where colloidal particles are formed, a comparison of soluble metal concentrations can be made with filtration through an ultrafiltration membrane. In all discussions and figures, pH refers to the reaction pH. It is controlled by a pH control device.

SULFIDE PRECIPITATION OF SINGLE METAL SOLUTION

Cd-Na_2S System

The primary reaction of cadmium ions to form cadmium sulfide is expressed by the following expression :

$$Cd^{2+} + S^{2-} \underset{<---}{\overset{--->}{}} CdS_{(s)} \qquad (31)$$

Previous studies (12) have indicated that the cadmium sulfide precipitation reached equilibrium in a short period of time. No significant change in cadmium concentration was observed at a reaction time of 5 minutes to 3 hours. Thus, experiments of this solution system were conducted to evaluate the effects of pH and the presence of interfering ions (such as, high chloride concentration).

Effect of pH

In order to evaluate the effects of pH on cadmium sulfide precipitation, a series of experiments was conducted with stoichiometric sulfide dosage (at S/Cd=1.0x) at various pH values. The residual cadmium concentration is compared with theoretical solubility and shown in Figure 8. There is no significant difference from the theoretical values at lower pH, but the residual concentration increases gradually with pH at higher pH.

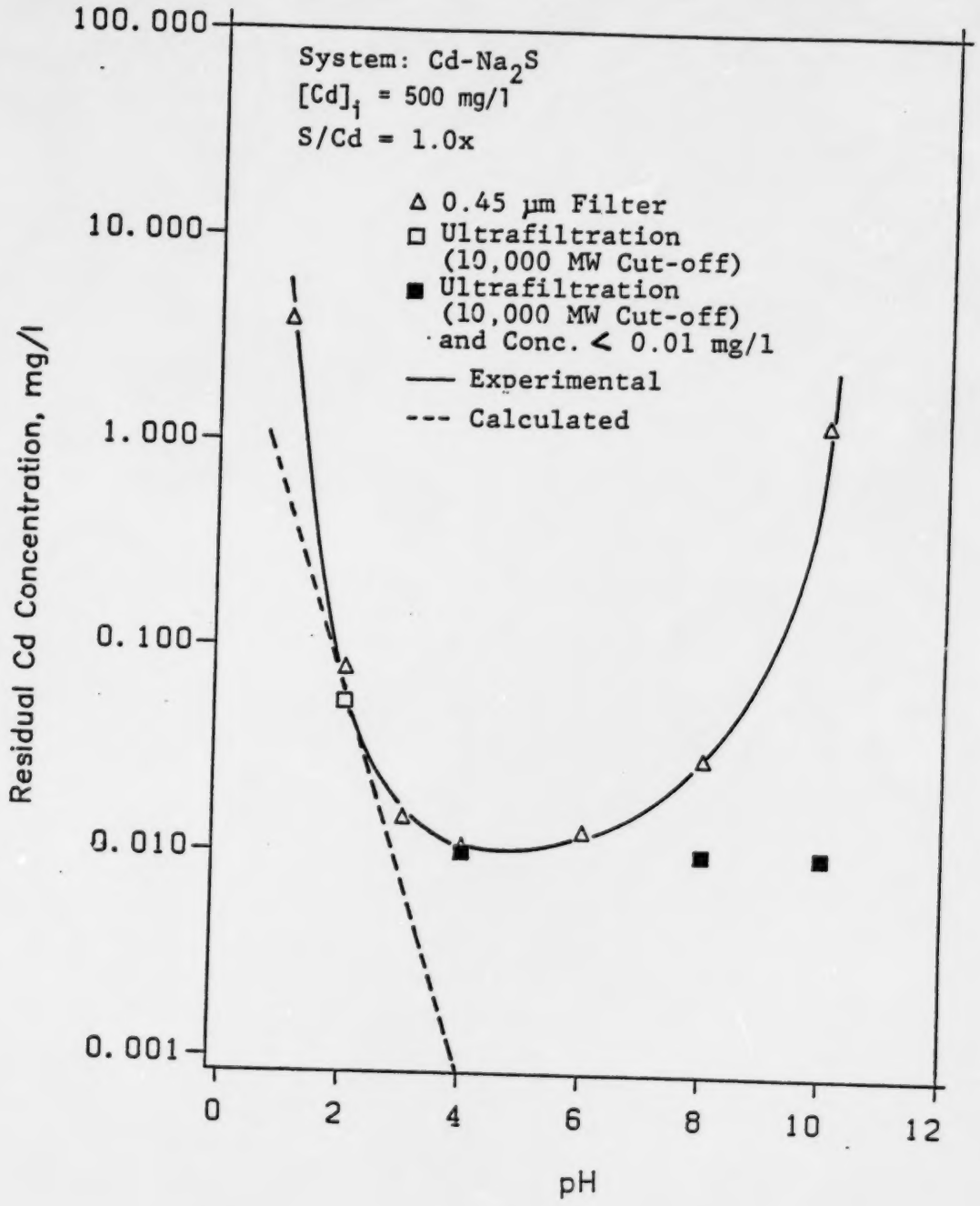

Figure 8. Effect of pH on CdS Precipitation in $Cd\text{-}Na_2S$ System.

A possible explanation is that the formation of fine particle precipitates occurred at the higher pH. Since these fine precipitates could pass through 0.45 μm filter and be counted as soluble cadmium, another filter with smaller porosity was used to prove the existence of fine particles. An ultrafilter, Amicon PM10 membrane (10,000 MW cut-off), was selected to refilter the filtrate obtained from a 0.45 μm filter. These data are represented by square symbols in Figure 8. Since the cadmium sensitivity of the Atomic Absorption Spectrophotometer was 0.01 mg/l, the data obtained below this level are presented by solid square symbols at 0.01 mg/l. As compared with the case of using 0.45 μm filter, the residual cadmium concentration obtained with ultrafiltrationwas lower at pH > 5. This indicates that the fine particle precipitates did contribute to the increase in residual concentration at higher pH. This type of comparison has never been reported in the literature.

To compare sulfide precipitation with hydroxide precipitation, a series of experiments was conducted at various pH values. The results are given in Figure 9. The difference in the residual cadmium concentration obtained by two different filters (0.45 μm filter and ultrafiltration membrane with 10,000 MW cut-off) is very small. In addition, both sets of experimental data fit well with the $Cd(OH)_2$ solubility curve calculated from the Ksp value (3.98×10^{-15} for $Cd(OH)_2$). A comparison between

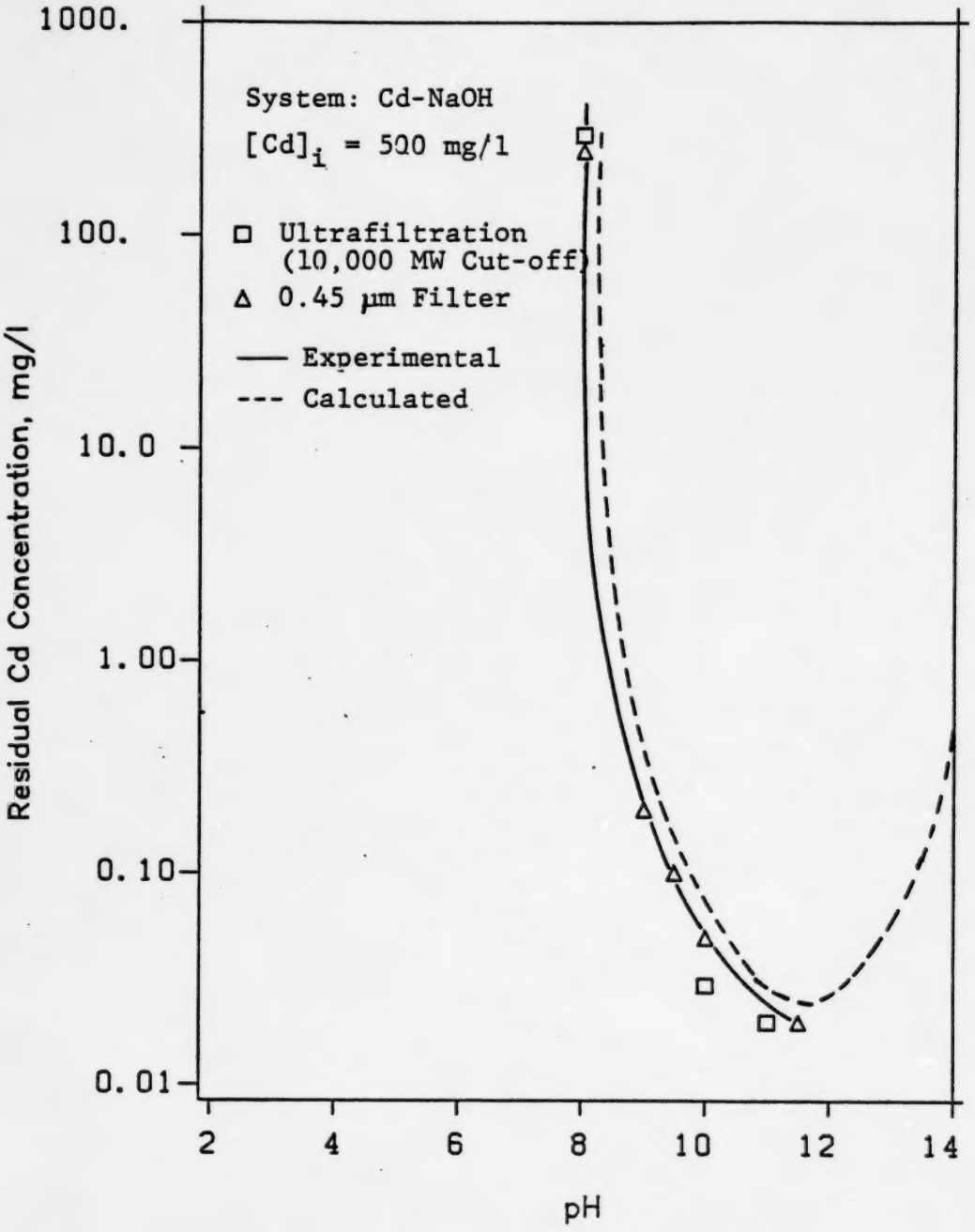

Figure 9. Comparison of Experimental and Calculated Results For $Cd(OH)_2$ Precipitation as a Function of pH.

Figure 8 and 9 indicates that sulfide precipitation with cadmium is highly effective over a broader pH range compared to the hydroxide precipitation.

Effect of high chloride concentration

Since some heavy metal wastewaters may contain a high chloride concentration (such as ion exchange regenerant solution) one study was conducted with cadmium in the presence of 3.0 wt% NaCl solution. It is well-known that chloride forms chlorometal complexes with some heavy metals. For example, with cadmium the following reactions may occur:

$$Cd^{2+} + Cl^{-} \quad \underset{\longleftarrow}{\longrightarrow} \quad CdCl^{+} \qquad K=26.3 \qquad (31)$$

$$Cd^{2+} + 2\ Cl^{-} \quad \underset{\longleftarrow}{\longrightarrow} \quad CdCl_2 \qquad K=83.2 \qquad (32)$$

The equilibrium constant for CdS formation is 10^{26} times higher than the chloride complex formation, thus one would expect very little interference from chloride ions. Table 3 shows negligible effect of chloride (3.0%) concentration on CdS precipitation.

Ni-Na_2S System

Previous studies (4) have indicated the strong dependence of reaction time on nickel sulfide precipitation in an open system (at pH < 10). With

TABLE 3

Effect of Chloride Ion on CdS Precipitation

System: Cd-Na_2S
$[Cd]_i$ = 500 mg/l
S/Cd = 1.0x
pH = 8.0

[Cl], wt%	Residual Cd Concentration, mg/l
0	0.07
3	0.03

experiments conducted in a closed system (under N_2 atmosphere), nickel sulfide precipitation was independent of reaction time. Moreover, it has been reported (16) that the fresh nickel sulfide precipitate is amorphous and thermodynamically unstable, and is called α-NiS. In the presence of oxygen, it may oxidize to generate polysulfides (such as, NiS_2 and Ni_3S_4), SO_4^{2-}, etc.

In accordance with the above investigations, the following reaction series is postulated:

$$Ni^{2+} + S^{2-} \;\rightleftharpoons\; \alpha\text{-}NiS_{(s)} \xrightarrow{O_2} \text{dissolution of NiS} \quad (33)$$

$$\alpha\text{-}NiS_{(s)} \xrightarrow{O_2} NiS_2 + Ni_3S_4 + SO_4^{2-} + \ldots$$

It assumes that the nickel sulfide precipitation is the primary reaction and is followed by some oxidation reactions to cause the dissolution of nickel sulfide precipitate. Experiments were conducted to evaluate the effects of pH, initial concentration, reaction time, and the presence of oxygen on nickel sulfide precipitation.

Effect of pH

For the purpose of evaluating the effects of pH, a series of experiments was conducted with an initial nickel concentration of 500 mg/l at stoichiometric sulfide dosage and at various pH levels. Results are shown in Figure 10 as a function of reaction time. The dissolution rate of

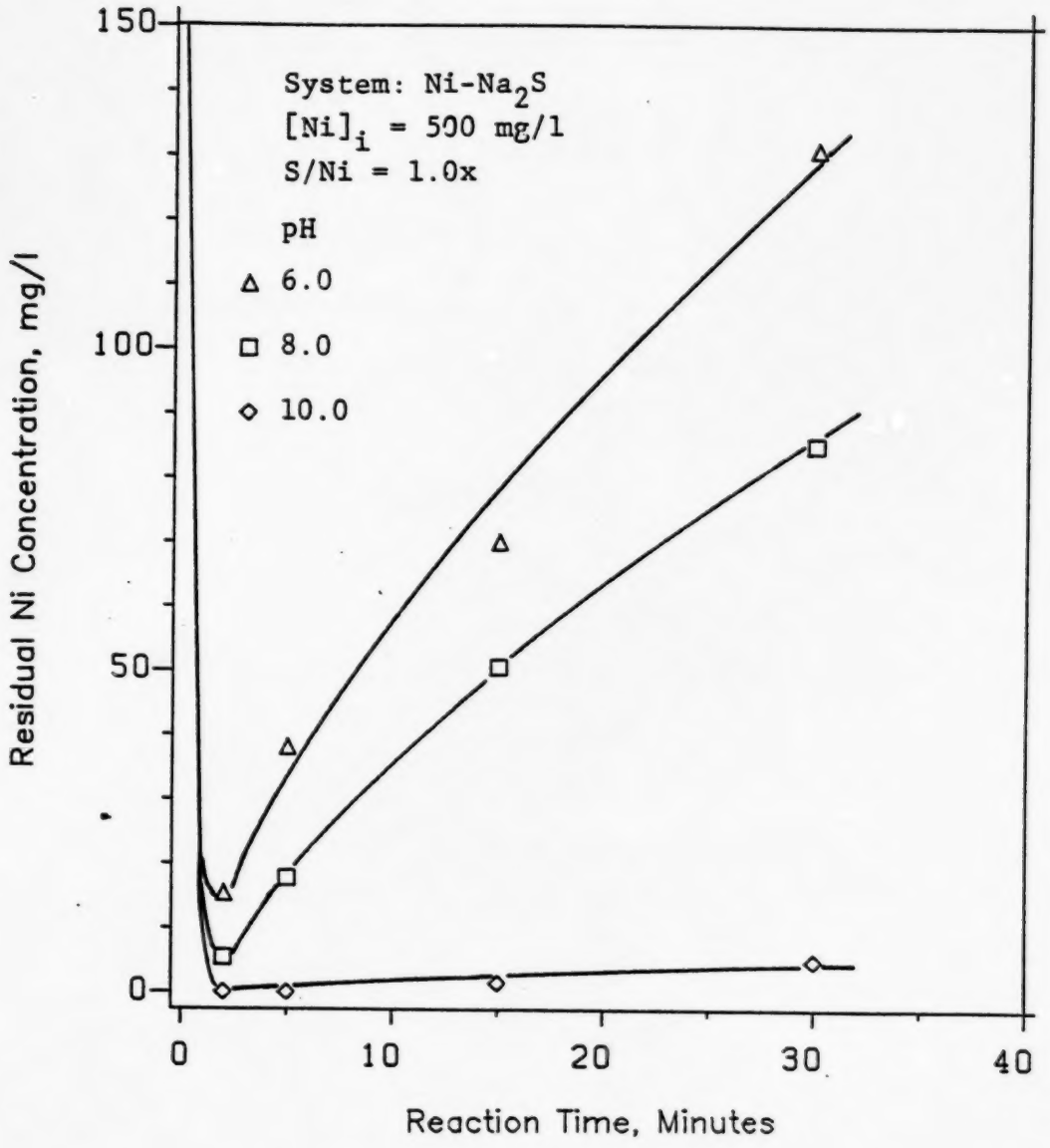

Figure 10 Effect of pH on NiS Precipitation as a Function of Time

nickel sulfide decreases as the pH value increases. Thus, nickel sulfide dissolution has to be taken into consideration at the lower pH range. At higher pH range (pH > 10), nickel sulfide dissolution is negligible. These results agree with the results of previous studies (4, 12).

Effect of reaction time and initial concentration

In order to investigate the effects of reaction time and initial concentration on this system, a series of experiments was carried out with stoichiometric sulfide dosage for various initial nickel concentrations. Since no significant nickel sulfide dissolution was observed at pH > 10, the pH value for this study was set at 6.0. The results are given in Figure 11. It shows the residual nickel concentration is not only a function of reaction time but also a function of initial nickel concentration.

For the 50 mg/l initial concentration run, the figure shows that about 80% of the nickel was soluble at a reaction time of 30 minutes. It may happen that the nickel sulfide dissolves completely in a long period of reaction time. Thus, an experiment with an initial concentration of 5000 mg/l was conducted for 24 hours under the same conditions to examine the long time effects. The residual nickel concentration was 334 mg/l at a reaction time of 24 hours; i.e. only about 6.6% of the nickel was soluble, as compared with the result of a

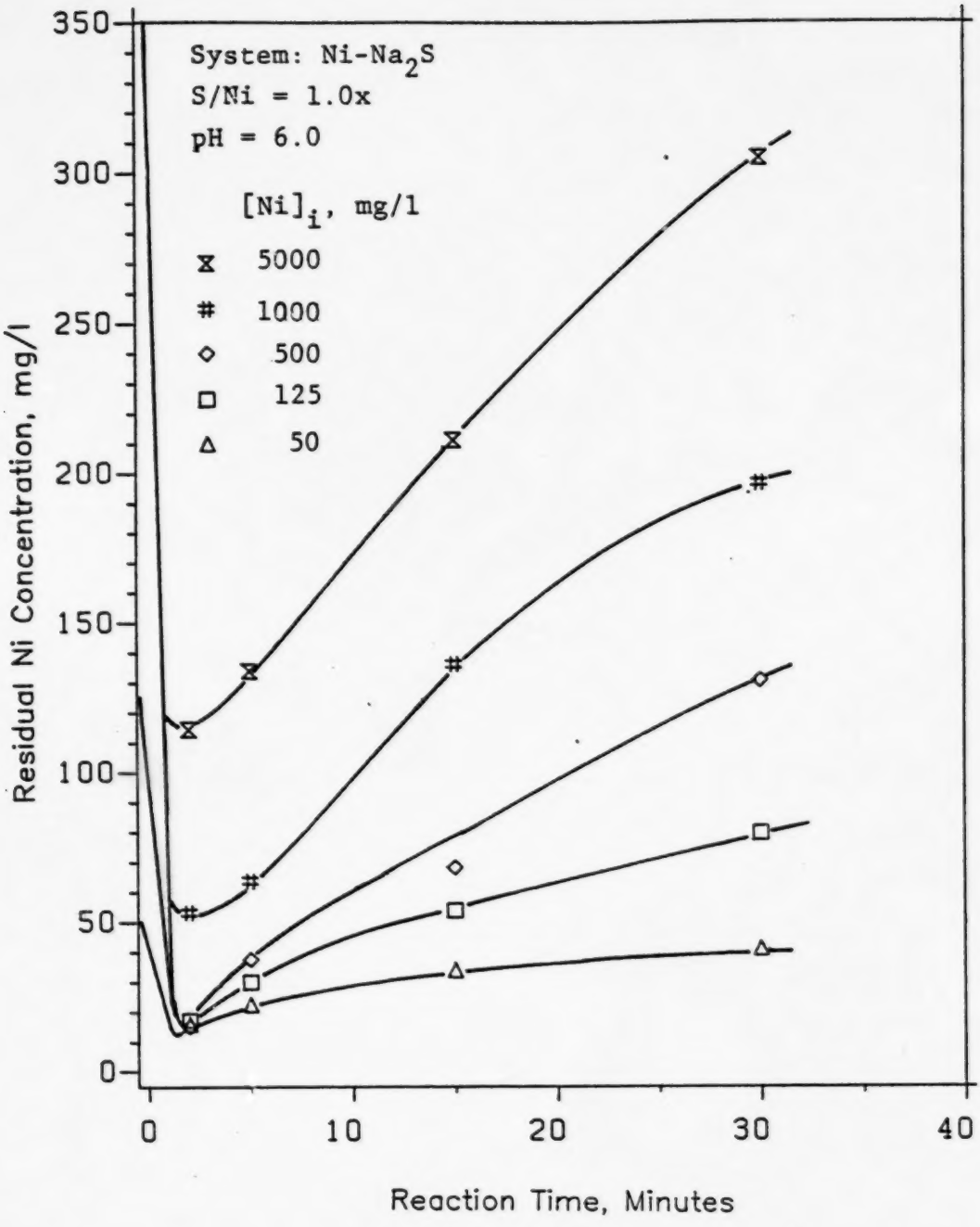

Figure 11. Effect of Reaction Time and Initial Concentration on NiS Precipitation.

30 minute reaction (6.1% of nickel was soluble). This indicates that the dissolution rate slowed down after a reaction time of 30 minutes. Hence, the precipitate of nickel sulfide does not dissolve completely even for a very long reaction time (for high initial nickel concentrations).

Converting the data of residual concentration from Figure 11, the extent of precipitation is presented in Figure 12. It can be observed that the extent of precipitation reaches a maximum value at a reaction time of about 2 minutes, then decreases with time. With an initial concentration of 125 mg/l, for instance, the extent of precipitation increased from zero to a maximum value of 89% within 2 minutes and then decreased gradually to 28% at a reaction time of 30 minutes. Thus for industrial treatment plant design (for nickel sulfide precipitation) with an open reactor system, a low detention time would be required.

The dotted line in Figure 12 represents the results of experiments conducted with an initial concentration of 125 mg/l in closed reactor systems (under N_2 atmosphere). It shows that the extent of precipitation in this case, after reaching the maximum, did not change with time.

From the above observations, it can be concluded that nickel sulfide precipitation is predominant at reaction times of less than 2 minutes. As soon as the nickel sulfide precipitate is formed, the oxidation of nickel

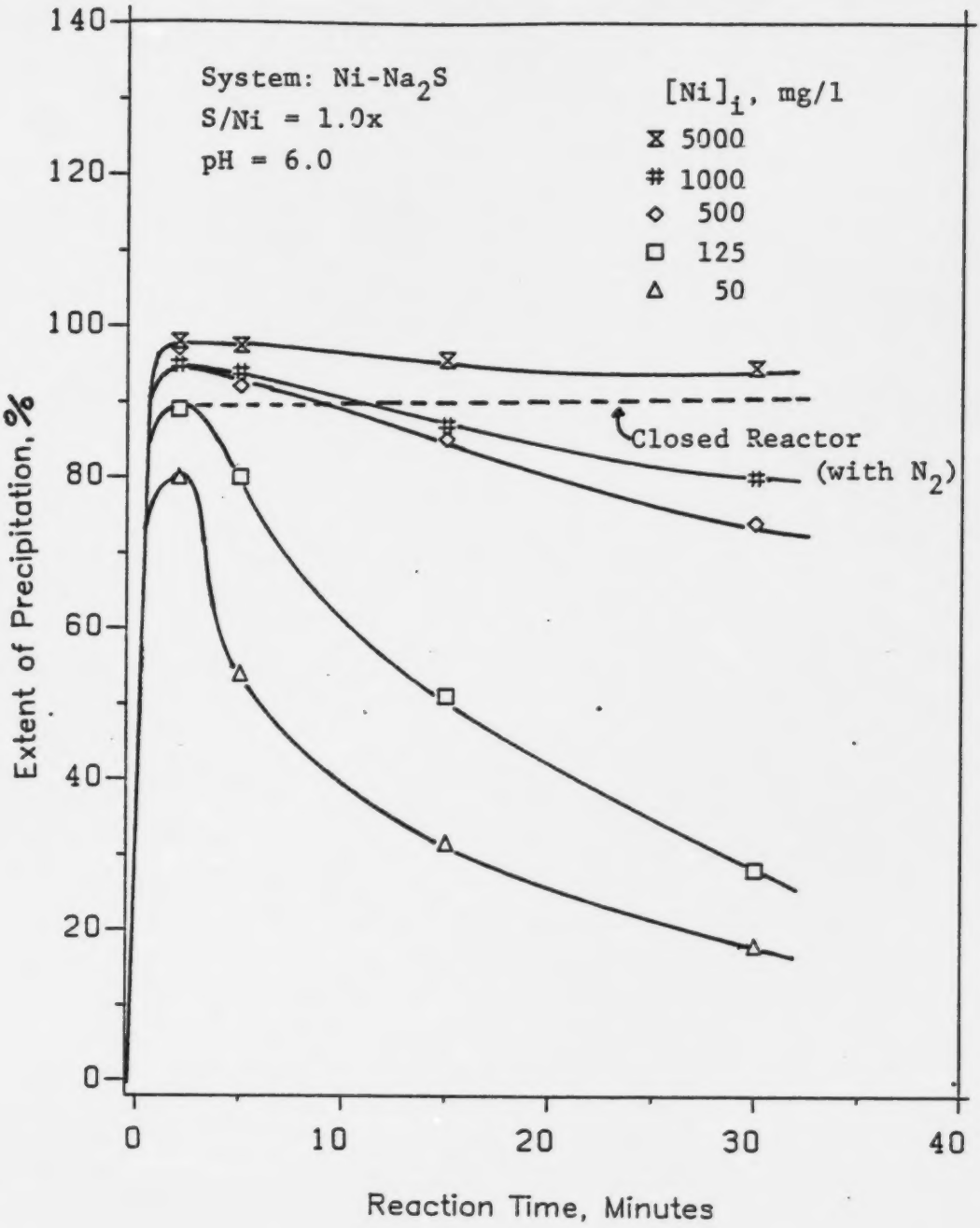

Figure 12. Effect of Reaction Time and Initial Concentration on the Extent of NiS Precipitation.

sulfide occurs and generates some unknown soluble species of nickel.

Co-Na_2S System

Cobalt was chosen because the systems of cobalt and nickel precipitation with sulfide resemble each other. They both belong to the same group (group VIII) in the Periodic Table. Similarly, the fresh precipitate of cobalt sulfide is also in α form which is amorphous and unstable. The solubility product of CoS is slightly higher than that of NiS (Table 1).

Experiments were conducted in solutions containing 125 mg/l of cobalt by adding a stoichiometric sulfide dosage at pH 6.0. In comparison with nickel, Figure 13 shows the residual metal concentration as a function of time. Essentially, the precipitation behavior of cobalt is similar to that of nickel in an open system. In other words, the dissolution of cobalt sulfide also occurs.

Since no nickel sulfide dissolution was observed in the closed system (under N_2 atmosphere), similar experiments was conducted with cobalt for comparison. Results for a closed system (under N_2 atmosphere), are also presented in Figure 13. It shows that a small dissolution of cobalt sulfide still occurred in a closed system (under N_2 atmosphere) but that the rate of dissolution was much lower than with the open reactor system.

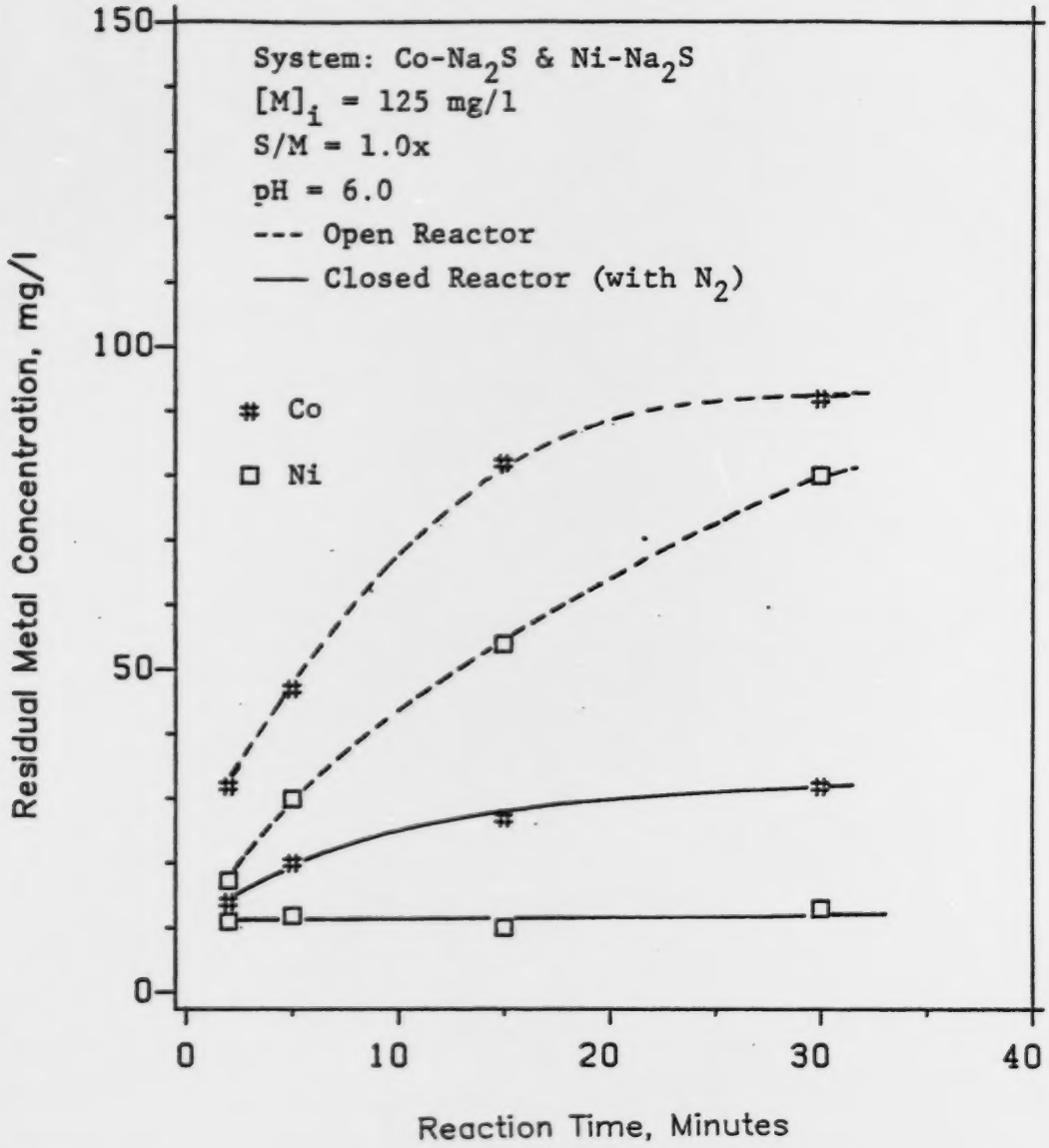

Figure 13. Comparison of CoS and NiS Precipitation in Two Reactor Systems (Open or Closed).

SULFIDE PRECIPITATION OF SOLUTIONS CONTAINING MULTI-METAL IONS

Additional studies were carried out in solutions containing more than one metal ion, to examine the interactions between different metal ions, and to observe the possible differences in individual metal sulfide precipitations. Previous studies (12) have indicated that the presence of nickel ions would affect the sulfide precipitation behavior of cadmium. Thus, most of the multi-metal solution systems being studied were nickel containing systems.

Ni-Zn-Na_2S System

Experiments were conducted to evaluate the effects of pH, reaction time, and Ni/Zn molar ratio. The sulfide dosage used in this system was stoichiometric to the total molarity of metals (at S/M_T=1.0x).

Effect of pH

A series of experiments was conducted at various pH values to evaluate the effects of pH on the precipitation behavior of the metals in a Ni-Zn-Na_2S system. Results of experiments conducted with a molar Ni/Zn=1.0 ($[Zn]_i$=125 and $[Ni]_i$=112 mg/l) are given in Figure 14. Results of corresponding single metal systems with the same initial

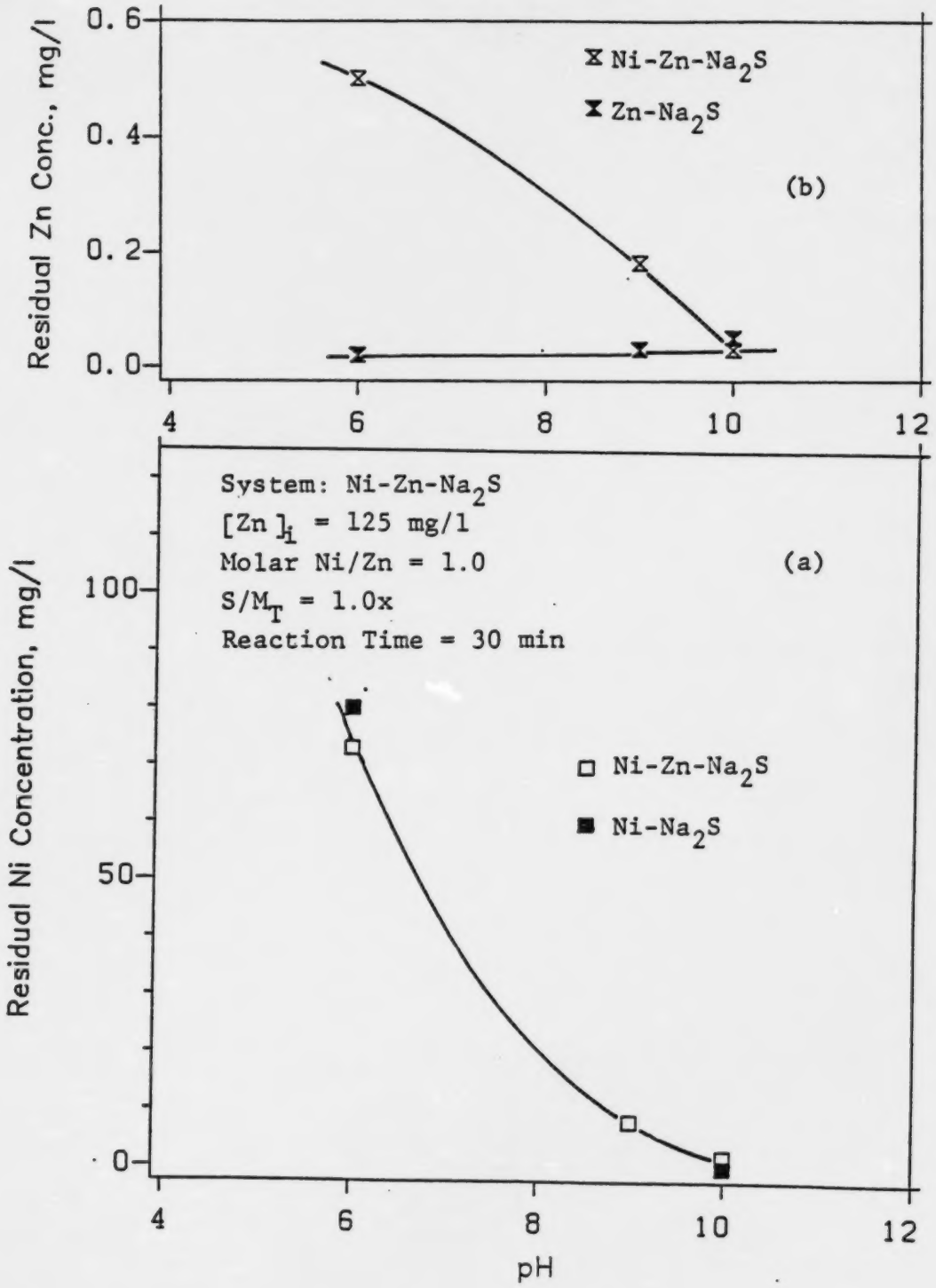

Figure 14 Effect of pH on (a) NiS and (b) ZnS Precipitation in Ni-Zn-Na_2S System

metal concentration are also given in Figure 14 for comparison. The nickel behavior in the mixed solution system was similar to that in single metal case; i.e. the nickel dissolution occurred at pH < 10 for both cases. However, the residual zinc concentration (at pH < 10) was higher (at a mixing time of 30 minutes) in the mixed metal solution system compared with the single metal case. This indicates that the interactions between nickel and zinc affect the precipitation behavior of zinc. It is possible that a coprecipitate may form in mixed metal systems.

Effect of reaction time and Ni/Zn molar ratio

Preliminary studies of the pH effects on Ni-Zn mixed metal solution systems showed that no metal sulfide dissolution occurred at pH > 10. Thus a series of experiments was conducted at pH < 10 (pH 6.0) to evaluate the effects of reaction time. With a Ni/Zn molar ratio of one, results are shown in Figure 15 as a function of time. As expected, the precipitation behavior of nickel in this mixed metal system was similar to the single metal case with the same initial concentration, but the precipitation behavior of Zn was affected. The residual concentration in the mixed metal solution system increased slightly with time while no dissolution of zinc sulfide occurred in the single metal case.

Since the zinc sulfide dissolution rate was considerably lower at molar Ni/Zn=1.0, the following

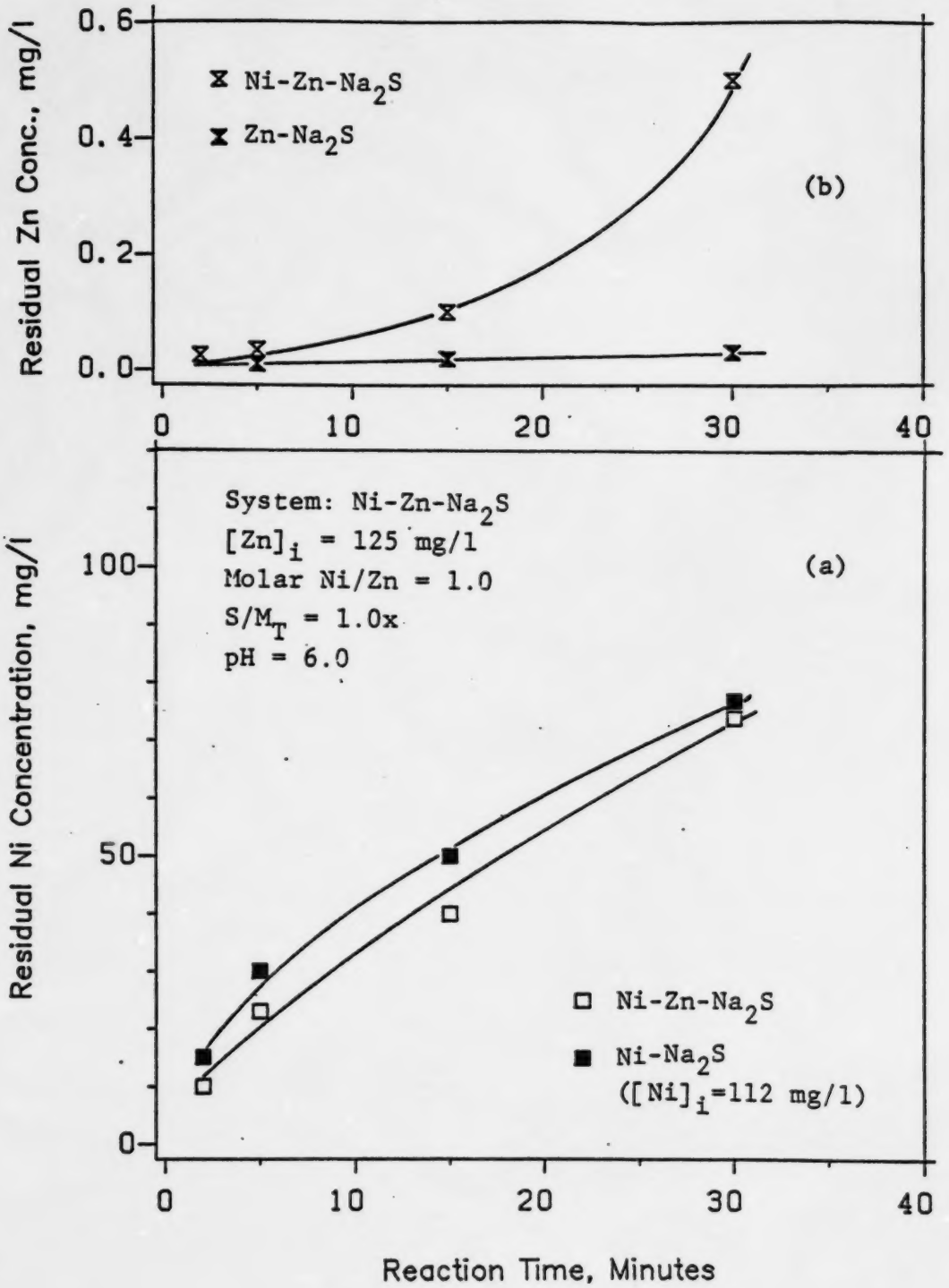

Figure 15 Effect of Reaction Time on (a) NiS and (b) ZnS Precipitation in Ni-Zn-Na_2S System

experiments were conducted at a fixed zinc concentration ($[Zn]_i$=125 mg/l) and with various Ni/Zn molar ratios to evaluate the Ni/Zn molar ratio effects. Figure 16 presents the results of pH 6.0 runs for a reaction time of 30 minutes. The residual concentration of both metals increased with the Ni/Zn molar ratio. The Ni/Zn molar ratio effects on the nickel behavior in the mixed metal system was similar to the initial concentration effects in the single metal system. The behavior change of zinc in the mixed metal system corresponds to the increased amount of soluble nickel. This may be due to the fact that nickel ions have catalytic effects on the zinc sulfide dissolution.

Effect of reactor system

Previous studies of Ni-Na_2S systems have indicated that the dissolution of nickel sulfide would be prevented if a closed reactor was used for pH < 10. Therefore, for the Ni-Zn-Na_2S system, some of the experiments were also conducted in closed reactor systems. Results for both open and closed reactor systems are presented in Figure 17(a) and (b) for experiments conducted at molar Ni/Zn=1.0 and at pH 6.0. Results for single metal systems are also plotted for comparison. With nickel, for both closed and open reactor systems, the results of the mixed metal solution systems were similar to those of their corresponding single metal solution systems.

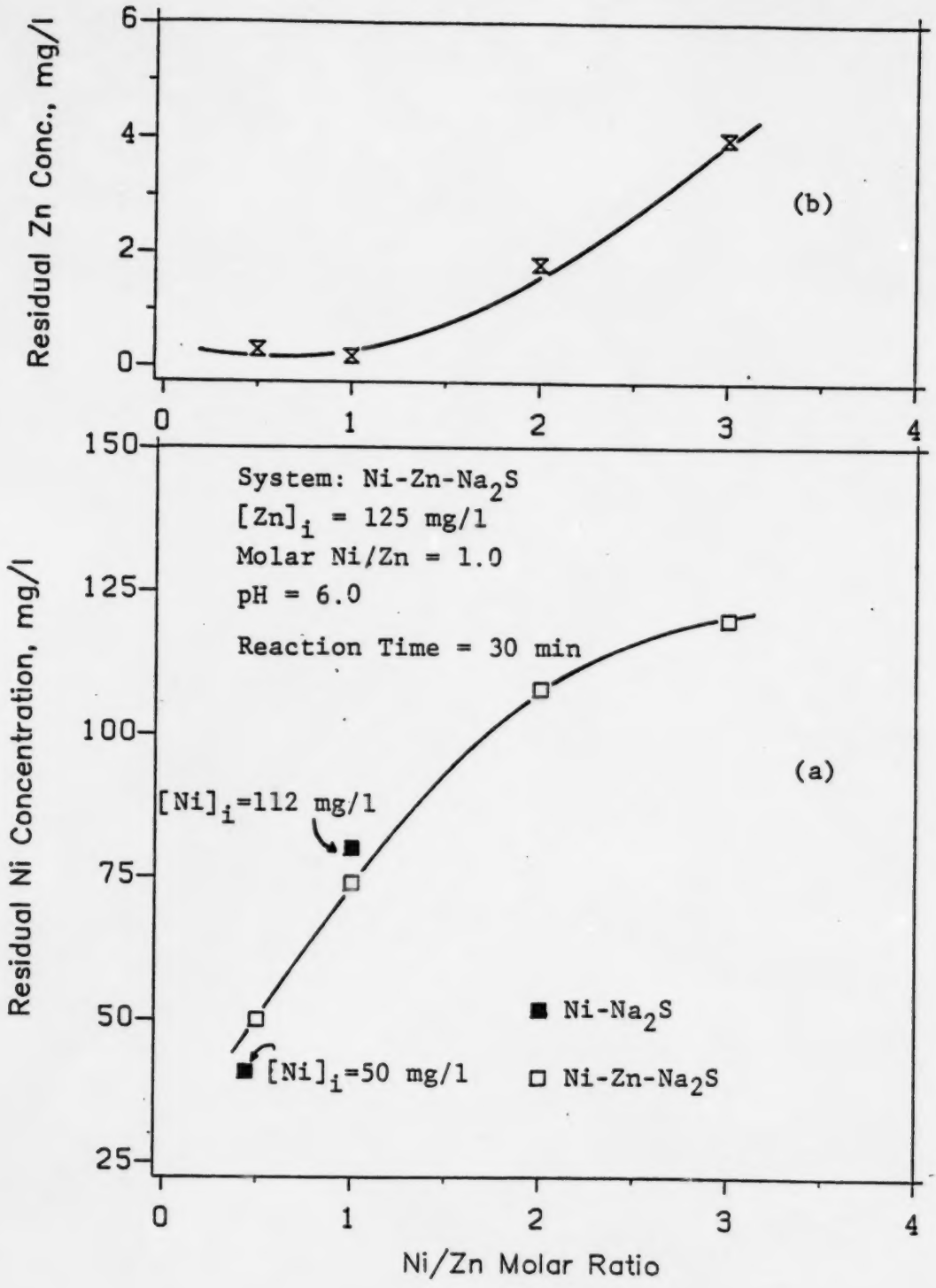

Figure 16 Effect of Ni/Zn Molar Ratio on (a) NiS and (b) ZnS Precipitation in Ni-Zn-Na_2S System

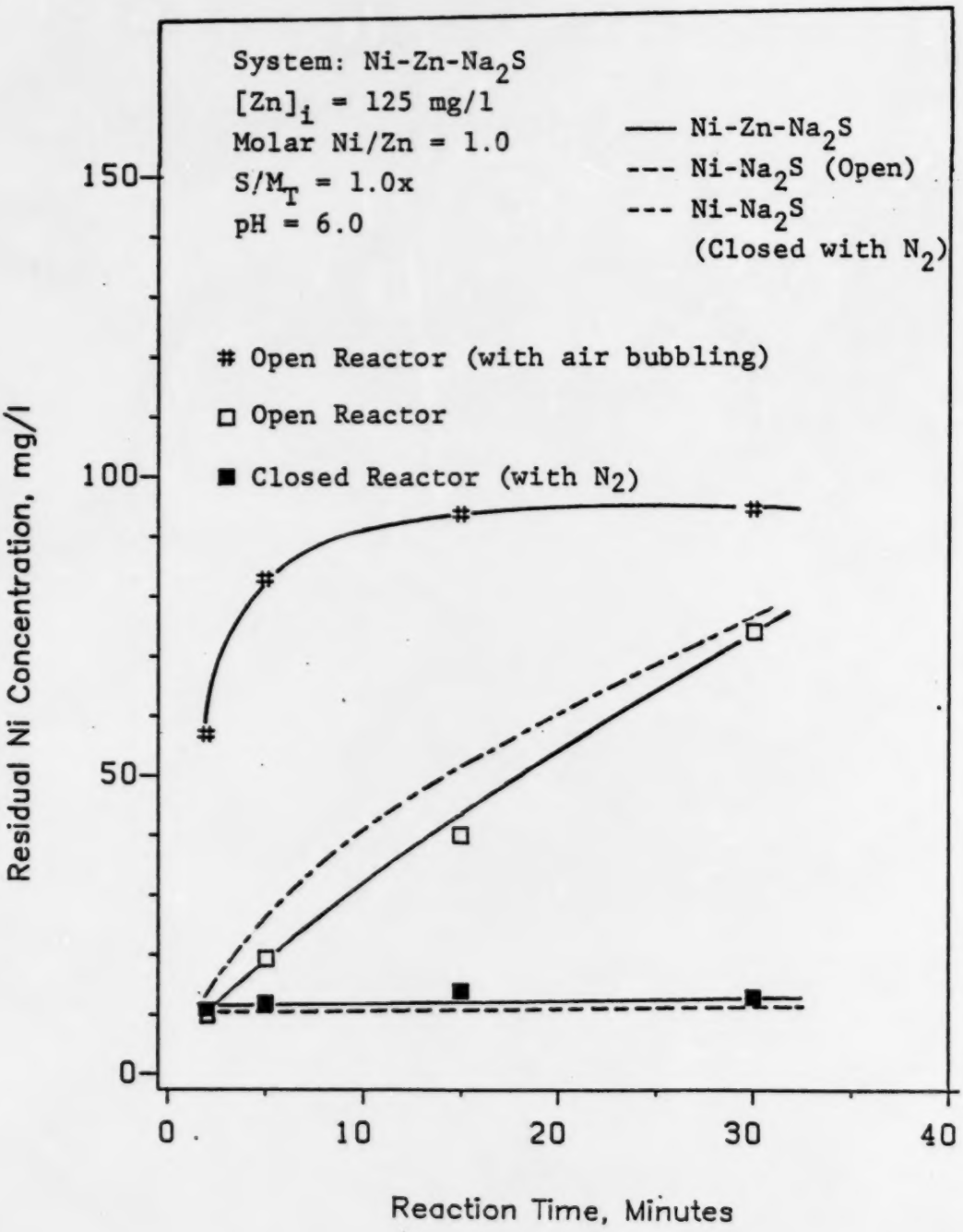

Figure 17(a). Effect of Reactor System on NiS Precipitation in Ni-Zn-Na_2S System.

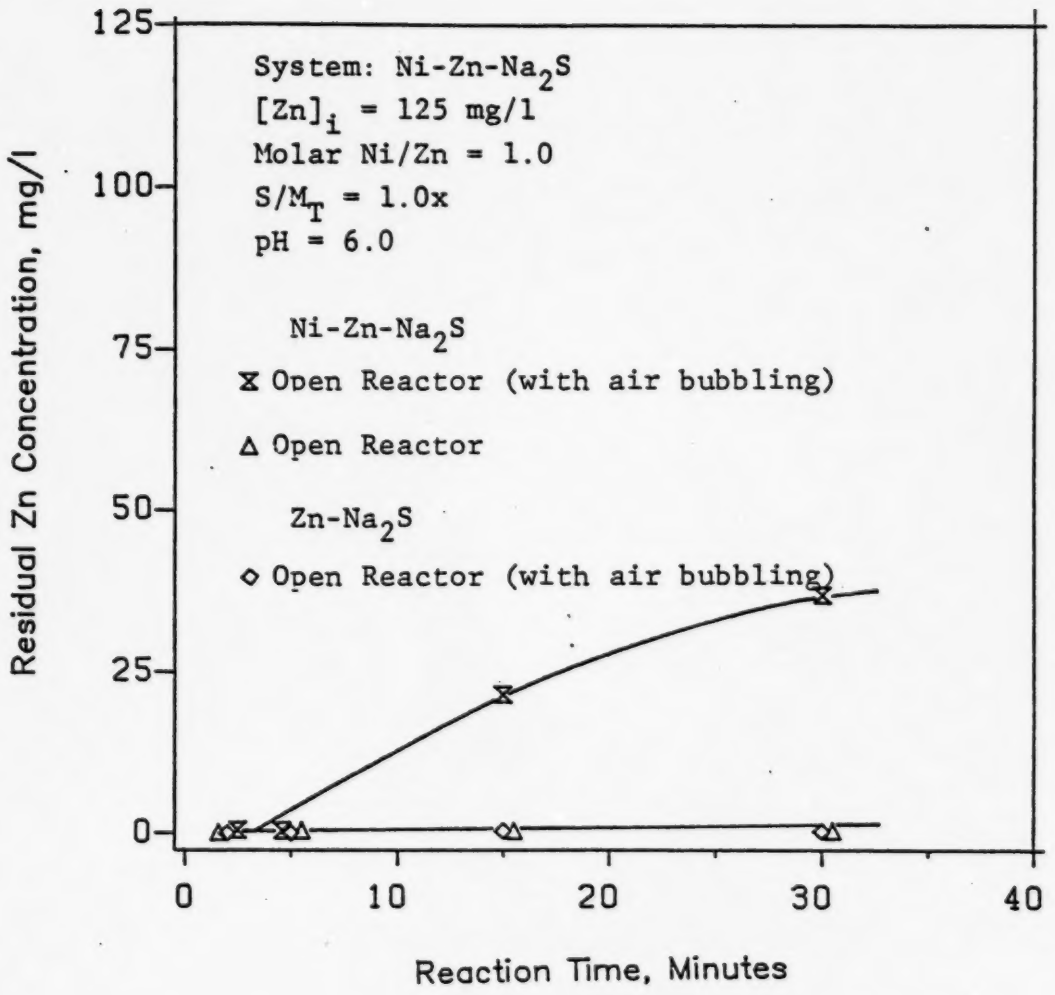

Figure 17 (b). Effect of Reactor System on ZnS Precipitation in Ni-Zn-Na_2S System.

In order to verify that the nickel sulfide dissolution may be enhanced by supplying more oxygen, further experiments were conducted in the open system with continuous air bubbling. Results are also given in Figure 17(a) and (b) for a Ni/Zn molar ratio of one. The nickel sulfide dissolution was much faster and reached equilibrium in a shorter period of time. Figure 17(b) shows that dissolution of zinc sulfide was enhanced in the Ni-Zn-Na_2S system with continuous air bubbling. Thus, the higher residual zinc concentration obtained in an open reactor system with continuous air bubbling corresponds with the catalytic effect of nickel ion on the oxidation of zinc sulfide.

Cu-Ni-Na_2S System

In order to examine the influences of the metal interactions in the Cu-Ni-Na_2S system, experiments were conducted at pH 6.0 and molar Ni/Cu=3.0 ($[Cu]_i$=125 mg/l and $[Ni]_i$=405 mg/l). Results are shown in Figure 18 for S/M_T=1.0x. The nickel concentration increased with time. Compared with the single nickel system, the extent of nickel sulfide dissolution was higher in the Cu-Ni-Na_2S system. Even in the presence of nickel, residual copper concentration was less than 0.01 mg/l indicating no effect of nickel on copper precipitation.

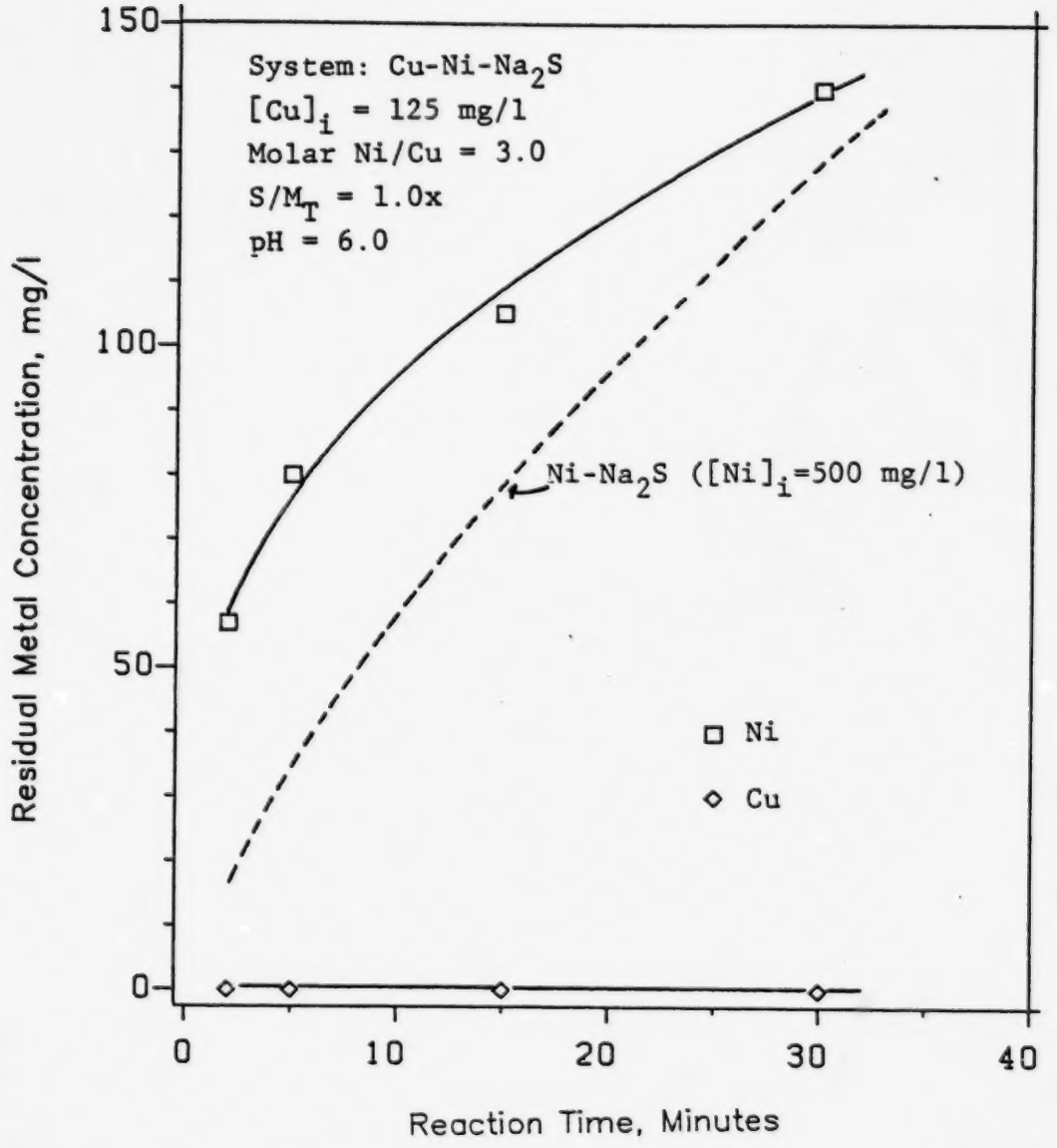

Figure 18. Effect of Reaction Time on CuS and NiS Precipitation in Cu-Ni-Na_2S System.

For the case of Cu-Na_2S system, the formation of colloidal copper sulfide precipitate has been reported in the literature (11) and the filtration through 0.45 μm filter resulted in residual concentration of 40-50 mg/l. The presence of nickel prevented the formation of colloidal copper sulfide precipitate as indicated by the residual concentration of less than 0.01 mg/l.

Cd-Cu-Zn-Na_2S System

This mixed metal solution system was chosen because all of the metal sulfide precipitations in their corresponding single metal solution systems were independent of time. Experiments were conducted in solutions containing cadmium, copper and zinc ions at pH 6.0.

Results are shown in Figure 19 as a function of time. With a sulfide dosage stoichiometric to the total molarity, the precipitation of metals was quite complete in this mixed metal system. For all three of these metals, the metal precipitation behavior in the mixed metal system was the same as in their corresponding single metal systems.

In order to examine the effectiveness of selective separation by varying the sulfide dosage, experiments were conducted with an arbitrarily selected sulfide dosage (at $S/M_T=0.22x$). Results in Figure 19 show that zinc and cadmium remained 100% soluble(in solution) and the copper

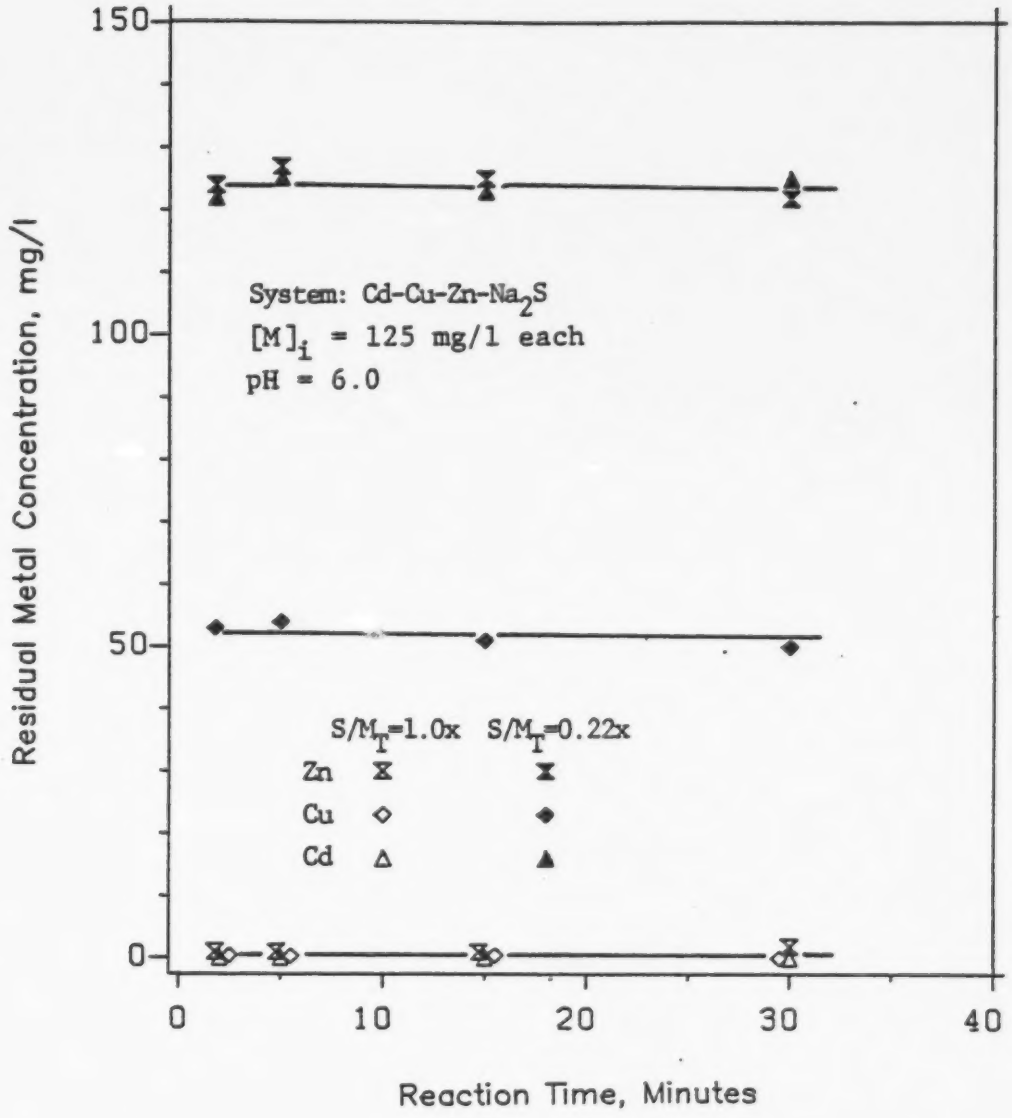

Figure 19 Effect of S/M_T Molar Ratio on Metal Sulfide Precipitation in Cd-Cu-Zn-Na_2S System

concentration was about 53 mg/l; i.e. 43% of copper remained soluble. These results were expected since the sulfide dosage added was only available for 56% of copper precipitation (at S/Cu=0.56x). Thus, the selective separation of metal is possible by only adjusting the sulfide dosage.

Cd-Cu-Ni-Zn-Na_2S System

Additional studies of sulfide precipitation were conducted on solutions containing four metals (cadmium, copper, nickel, and zinc) to evaluate the effects of nickel on the interactions between different metals. A series of experiments was conducted at S/M_T=1.0x and at pH 6.0. Figure 20 shows the results as a function of time.

In comparison with the single metal solution systems, the residual copper concentration was again < 0.01 mg/l in the mixed metal type system. The nickel behavior was similar in both systems (single or mixed metal) but the dissolution rate was higher in the mixed metal system. However, the behavior of zinc and cadmium changed in this mixed metal system.

The extent of precipitation was in the following order: CuS > CdS > ZnS > NiS; i.e. the reverse order of their corresponding solubility products. In other words, the extent of metal sulfide dissolutions corresponded with the solubility product.

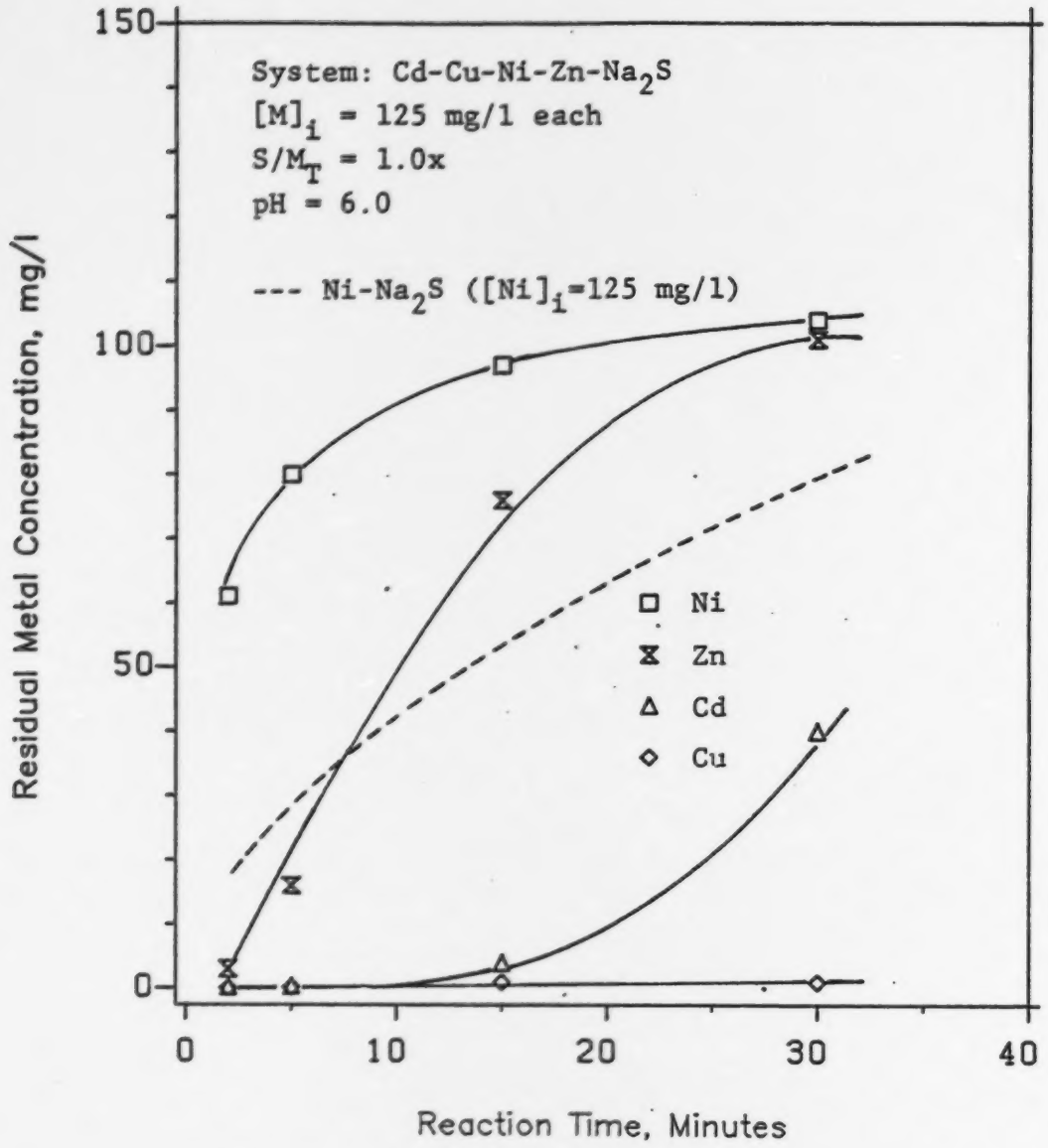

Figure 20 Effect of Reaction Time on Metal Sulfide Precipitation in Cd-Cu-Ni-Zn-Na_2S System

Further studies were conducted to evaluate the effectiveness of higher sulfide dosage (at S/M_T > 1.0x) on improving the precipitation of cadmium, zinc and nickel. The results are shown in Figure 21. The addition of excess sulfide dosage had no significant effect on zinc, copper and nickel precipitation. However, it was effective in improving the precipitation of cadmium. For example, the residual cadmium concentration dropped to 8 mg/l at S/M_T=1.5x while it was 40 mg/l at S/M_T=1.0x.

One experiment was conducted at high pH (pH 10.0) for the mixed metal system, and the results are shown in Table 4. It can be seen that all the metals, including nickel, were completely removed from the mixed metal system and no dissolution of metal sulfides occurred. These results are similar to those observed with single metal systems.

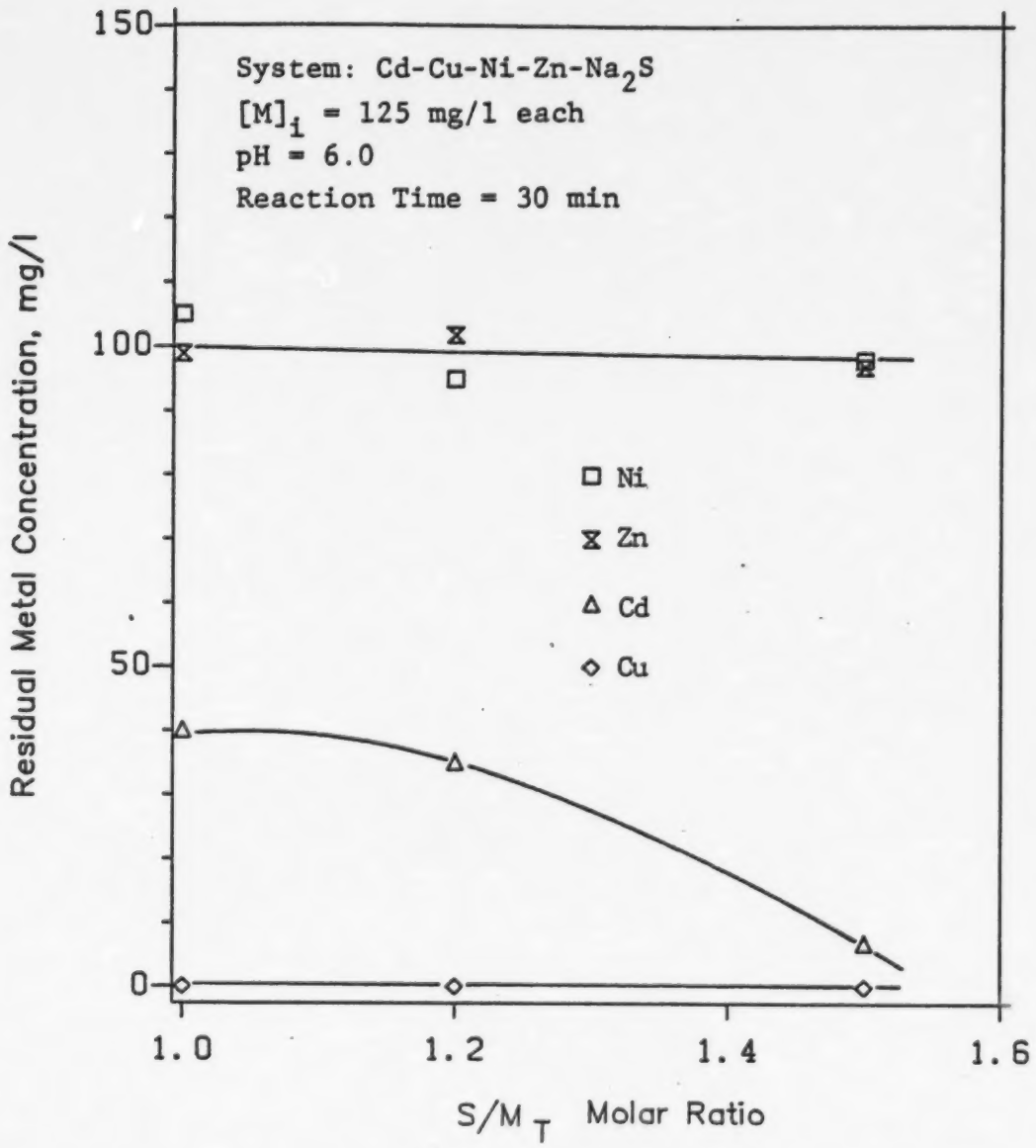

Figure 21 Effect of S/M_T Molar Ratio on Metal Sulfide Precipitation in Cd-Cu-Ni-Zn-Na_2S System

TABLE 4

Metal Sulfide Precipitation in
Cd-Cu-Ni-Zn-Na_2S System at pH 10

System: Cd-Cu-Ni-Zn-Na_2S
$[M]_i$ = 125 mg/l each
S/M_T = 1.0x
pH = 10.0

Metal	Residual Metal Concentration, mg/l	
	θ = 2 min	θ = 30 min
Cd	< 0.01	< 0.01
Cu	< 0.01	< 0.01
Ni	0.02	0.06
Zn	0.04	0.08

SELECTIVE METAL PRECIPITATION IN THE PRESENCE OF EDTA

In general, water streams that contain heavy metals may also have some chelating agents (such as EDTA, citrate, oxalate, etc.) present. Extensive studies were made by Ku (12) in evaluating the effects of some chelating agents (at low molar ratio of chelate/metal) on metal sulfide precipitation. It was reported that EDTA had the strongest effect on reducing the extent of sulfide precipitation of metals such as cadmium, copper, nickel, and zinc. By means of the variation in apparent stability constants (K'_{ML}) of metal-EDTA complex, it is possible to achieve selective precipitation by the addition of a proper amount of EDTA and by pH variation.

Cd-EDTA-Na_2S System

In order to evaluate the effects of reaction time, pH and EDTA/Cd molar ratio on cadmium sulfide precipitation in the presence of EDTA, experiments were conducted in solutions containing 125 mg/l cadmium and at stoichiometric sulfide dosage (at S/Cd=1.0x).

The reaction time (0-30 minutes) had no influence on the extent of precipitation. Results of the pH experiments are given in Figure 22. The trend in precipitation results agrees well with the change in apparent solubility constants. At pH < 4.0, the low K'_{ML} value corresponds

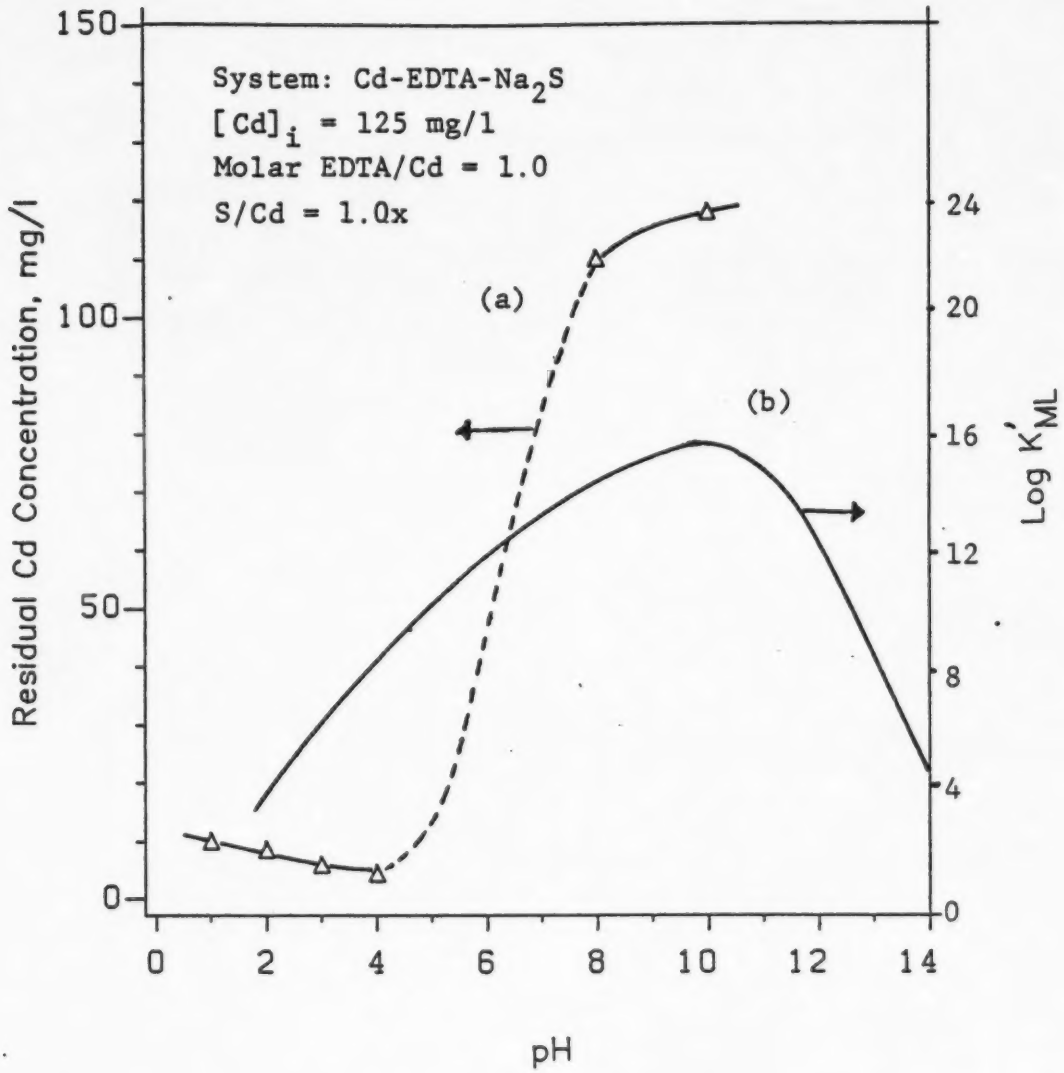

Figure 22. Effect of pH on (a) CdS Precipitation in Cd-EDTA-Na_2S System and (b) Apparent Stability Constant of Cd-EDTA Complex.

to a high degree of metal precipitation. While at pH > 8, almost 90% cadmium remained soluble. This is in contrast to the precipitation of cadmium with $Ca(OH)_2$ where effective precipitation can only be obtained at pH > 12.

A series of experiments was also conducted at pH 8.0 to evaluate the effects of lower EDTA/Cd molar ratio on cadmium sulfide precipitation. Figure 23 shows the results as a function of EDTA/Cd molar ratio. At pH 8.0 where Cd-EDTA complex is highly stable, increased precipitation occurs only at EDTA/Cd molar ratio < 0.2. Of course, in the absence of EDTA (Figure 8) effective precipitation could be obtained over a broad pH range.

Ni-Zn-EDTA-Na_2S System

The studies of Ni-Zn-Na_2S system showed selective precipitation of metals could be achieved successfully by long term reaction or by using an open reactor at pH < 8.0. The addition of EDTA may be a more effective alternative to accomplish the same purpose.

A series of experiments was carried out in solutions containing nickel, zinc and EDTA at pH 6.0. In these experiments, the sulfide dosage was stoichiometric to the total molarity of the metals. These results are shown in Figure 24 as a function of time. It can be seen that the separation of nickel from zinc was more satisfactory in the presence of EDTA even at short reaction times. Since

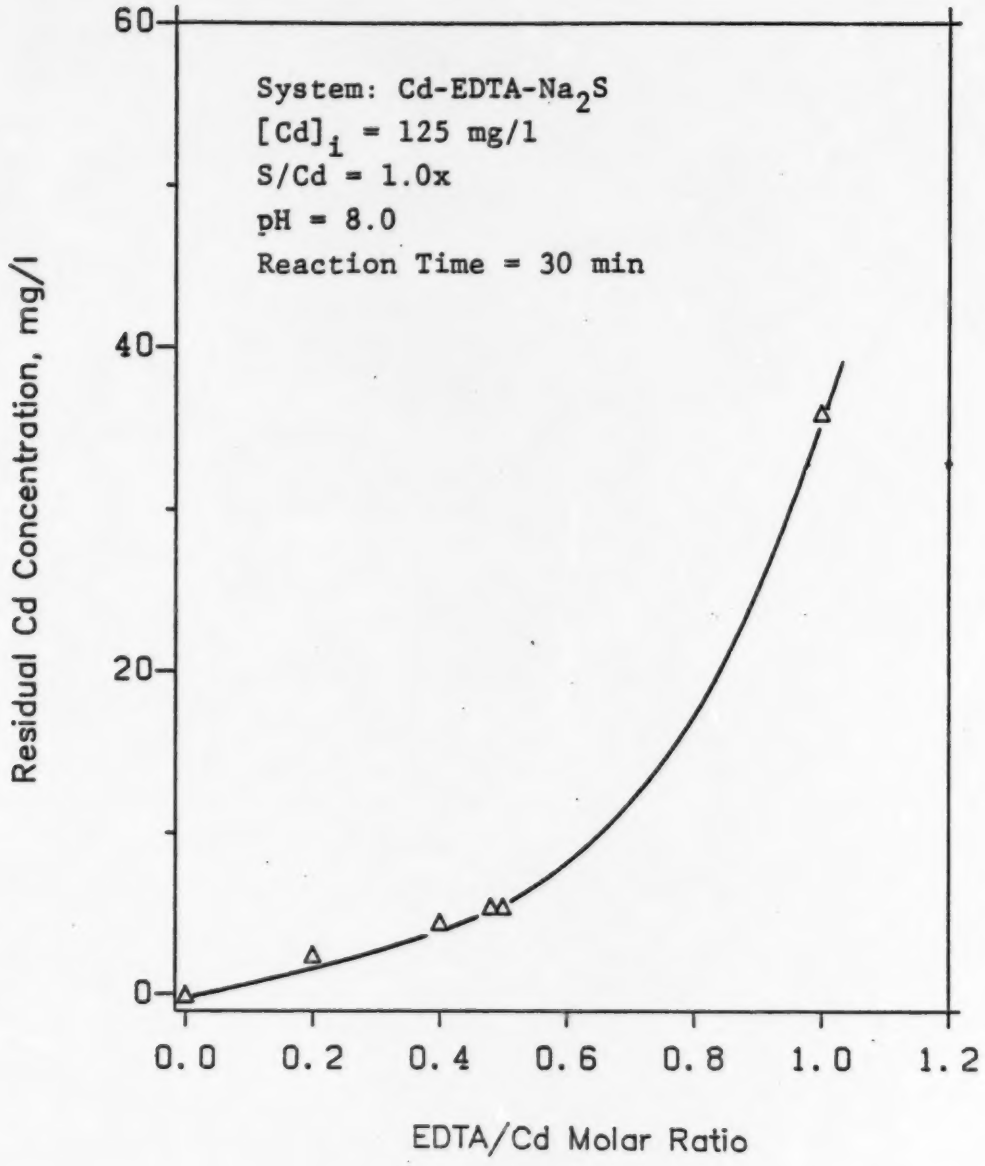

Figure 23. Effect of EDTA/Cd Molar Ratio on CdS Precipitation in Cd-EDTA-Na_2S System.

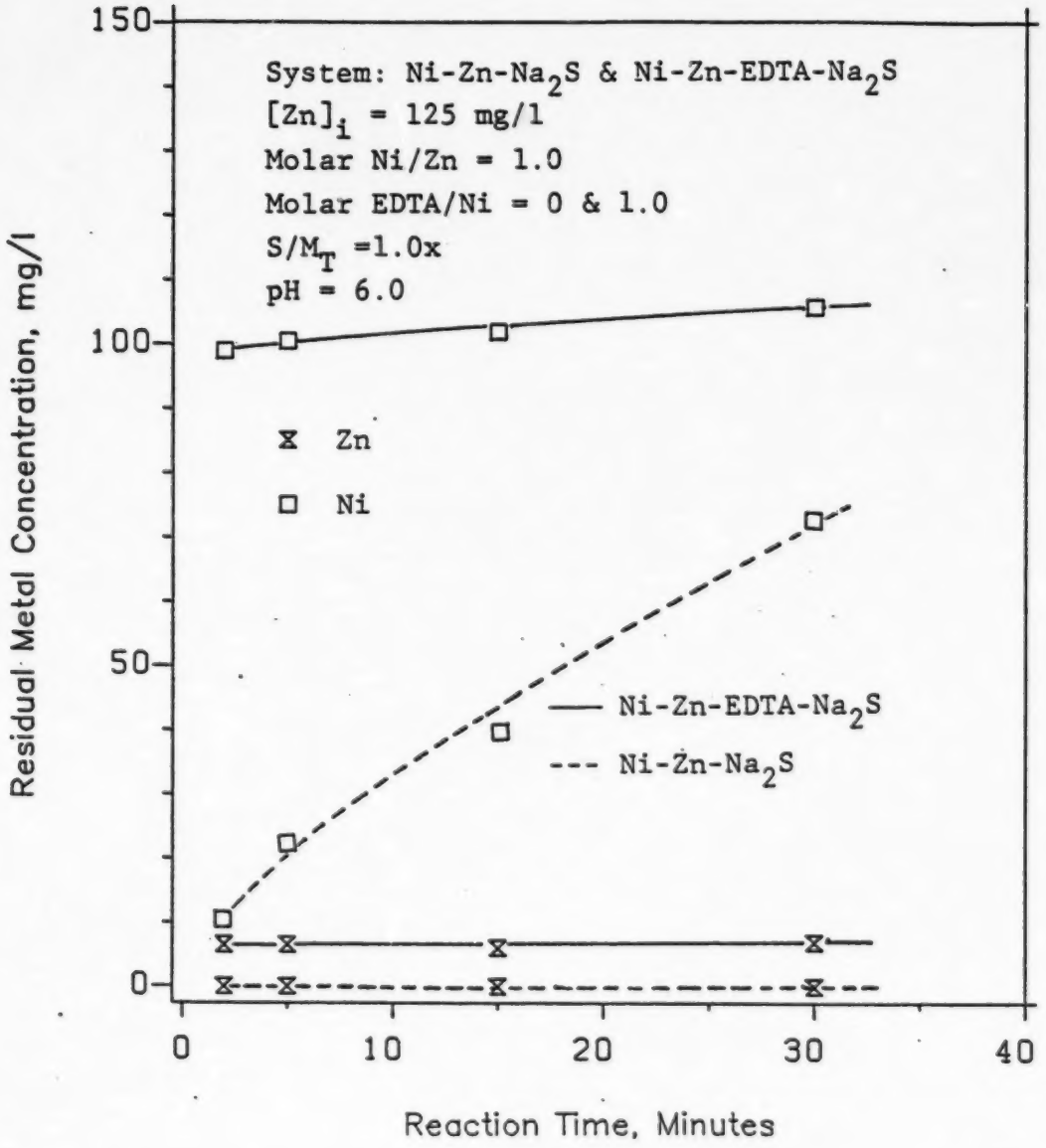

Figure 24. Comparison of Metal Sulfide Precipitation Between Ni-Zn-Na_2S and Ni-Zn-EDTA-Na_2S Systems.

EDTA formed a more stable complex with nickel than with zinc (K'_{ML} Ni/K'_{ML} Zn=1.2 at pH 6.0) the presence of EDTA resulted in the increase of nickel concentration more than that of zinc.

Figure 25 shows the results of experiments which were conducted to examine the effects of higher EDTA/Ni molar ratio. It can be shown that the EDTA/Ni molar ratio is an important factor effecting the separation. For the purpose of separation, the results of experiments with EDTA/Ni molar ratio of one were considered better than those where the molar ratio was two because of reduced zinc precipitation.

In an attempt to examine the effects of oxygen on selective metal separation processes, some experiments were made in a closed reactor system (under N_2 atmosphere). Results compared with those of open reactor system are shown in Figure 26 for the EDTA/Ni molar ratio of one. The results of both reactor systems were about the same. It indicates that the oxygen effects were insignificant in the presence of EDTA. Hence, the metal separation in terms of zinc is satisfactory at a EDTA/Ni molar ratio of one for either open or closed reactor systems when compared with the case without EDTA.

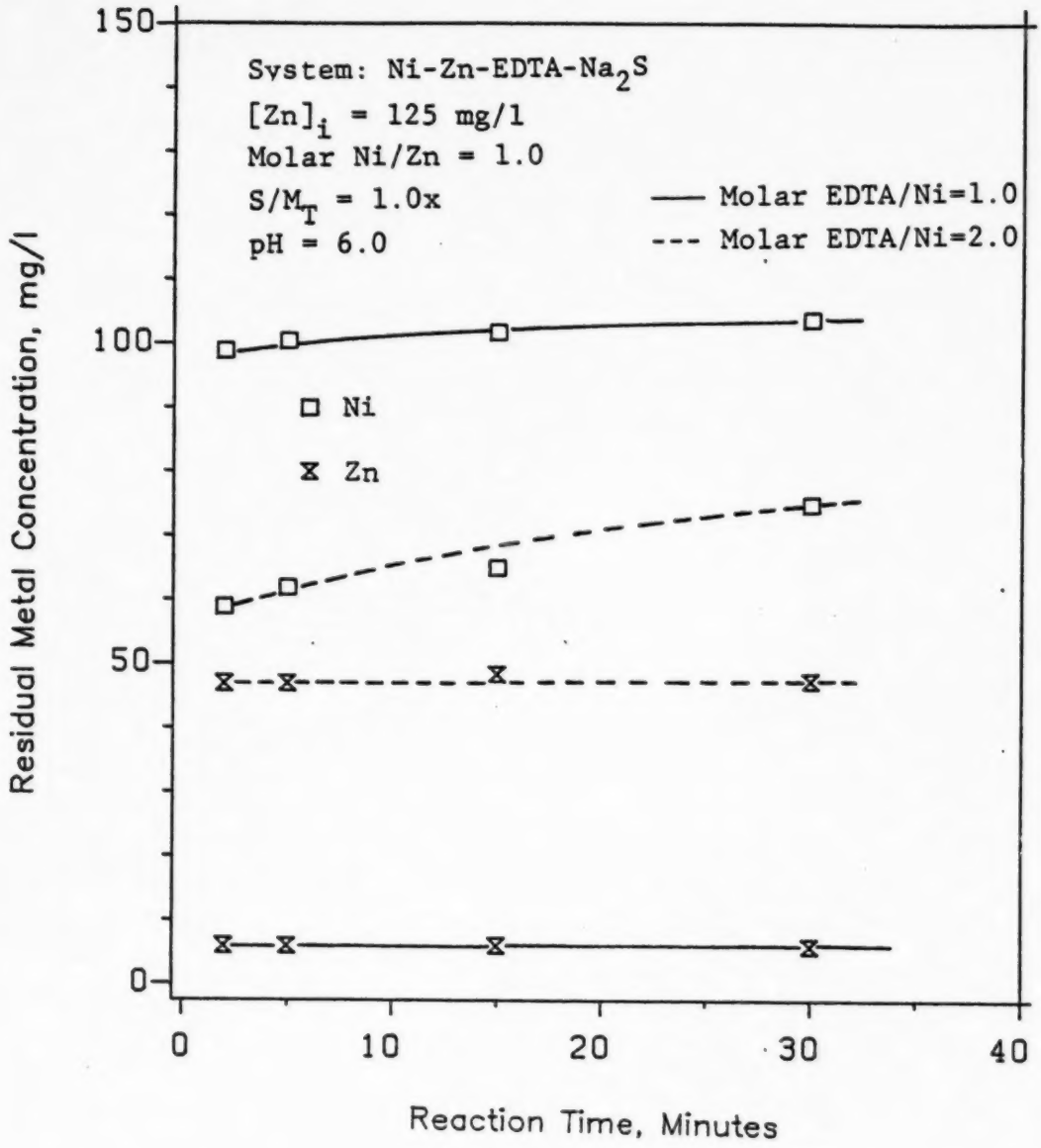

Figure 25. Effect of EDTA/Ni Molar Ratio on Metal Sulfide Precipitation in Ni-Zn-EDTA-Na_2S System.

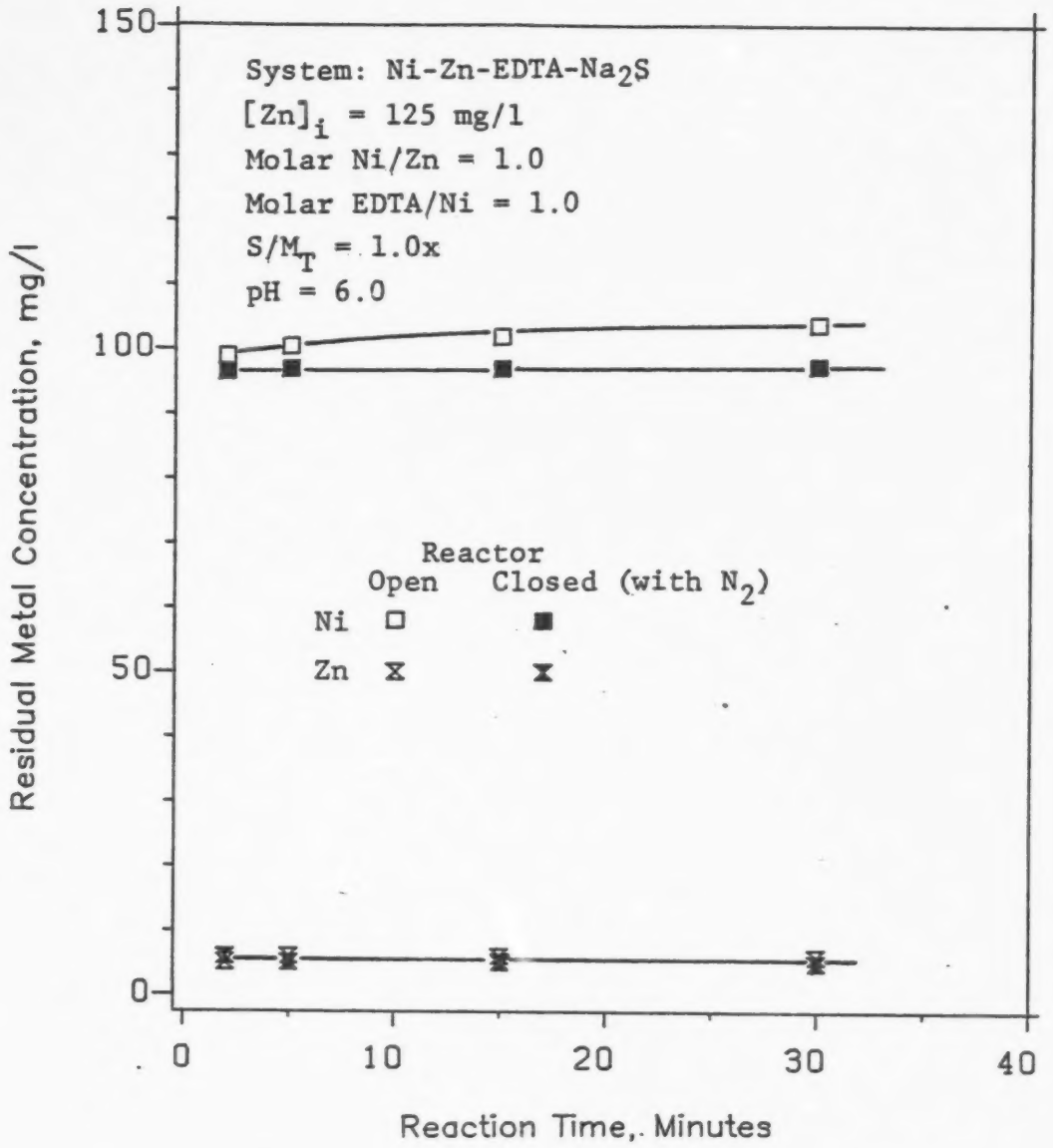

Figure 26. Effect of Reactor System on Metal Sulfide Precipitation in Ni-Zn-EDTA-Na_2S System.

Zn-Ca-EDTA-Na_2S System

Previous studies have indicated that the extent of zinc sulfide precipitation would be reduced in the presence of high concentration of EDTA (12). Calcium was added in the system containing EDTA so that it could compete with Zn-EDTA reaction. By this method, it may reduce the relative amount of EDTA available to affect the extent of zinc precipitation.

Effect of reaction time

For the evaluation of the effects of reaction time, experiments were conducted with an initial zinc concentration of 125 mg/l, and at a EDTA/Zn molar ratio of one and a Ca/EDTA molar ratio of 20. The experimental results are given in Figure 27 as a function of time. The residual zinc concentration decreased with time. In the presence of high calcium, 72% of the original zinc was precipitated.

The results of experiments conducted at a Ca/EDTA molar ratio of 20 but without EDTA are also shown in Figure 27. Since the results are same as those of single zinc solution system, it can be concluded that calcium itself had no influence on zinc sulfide precipitation.

Effect of EDTA/Zn molar ratio

Figure 28 shows the effects of EDTA/Zn molar ratio on

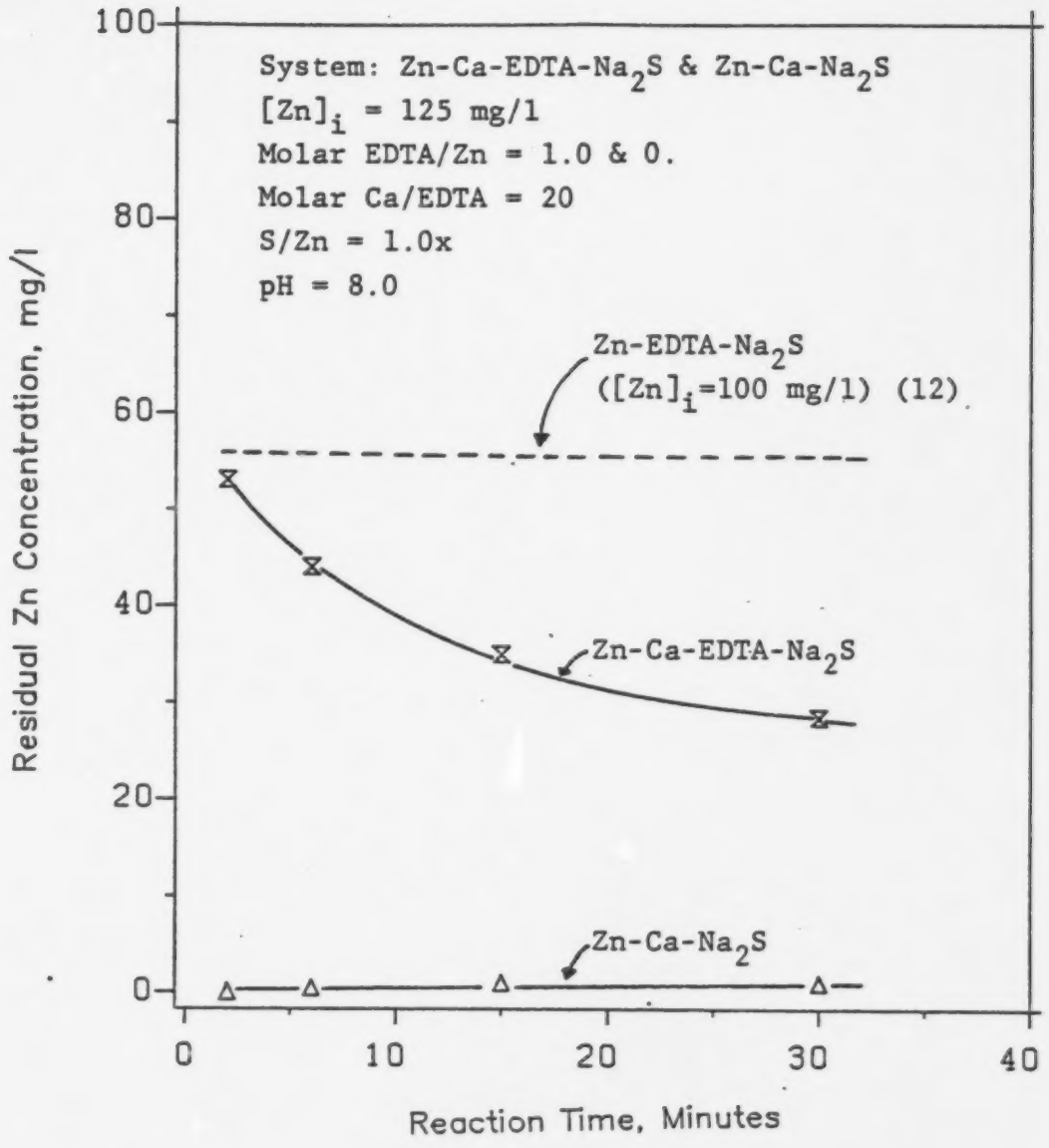

Figure 27. Comparison of ZnS Precipitation Among Zn-EDTA-Na_2S, Zn-Ca-EDTA-Na_2S & Zn-Ca-Na_2S Systems.

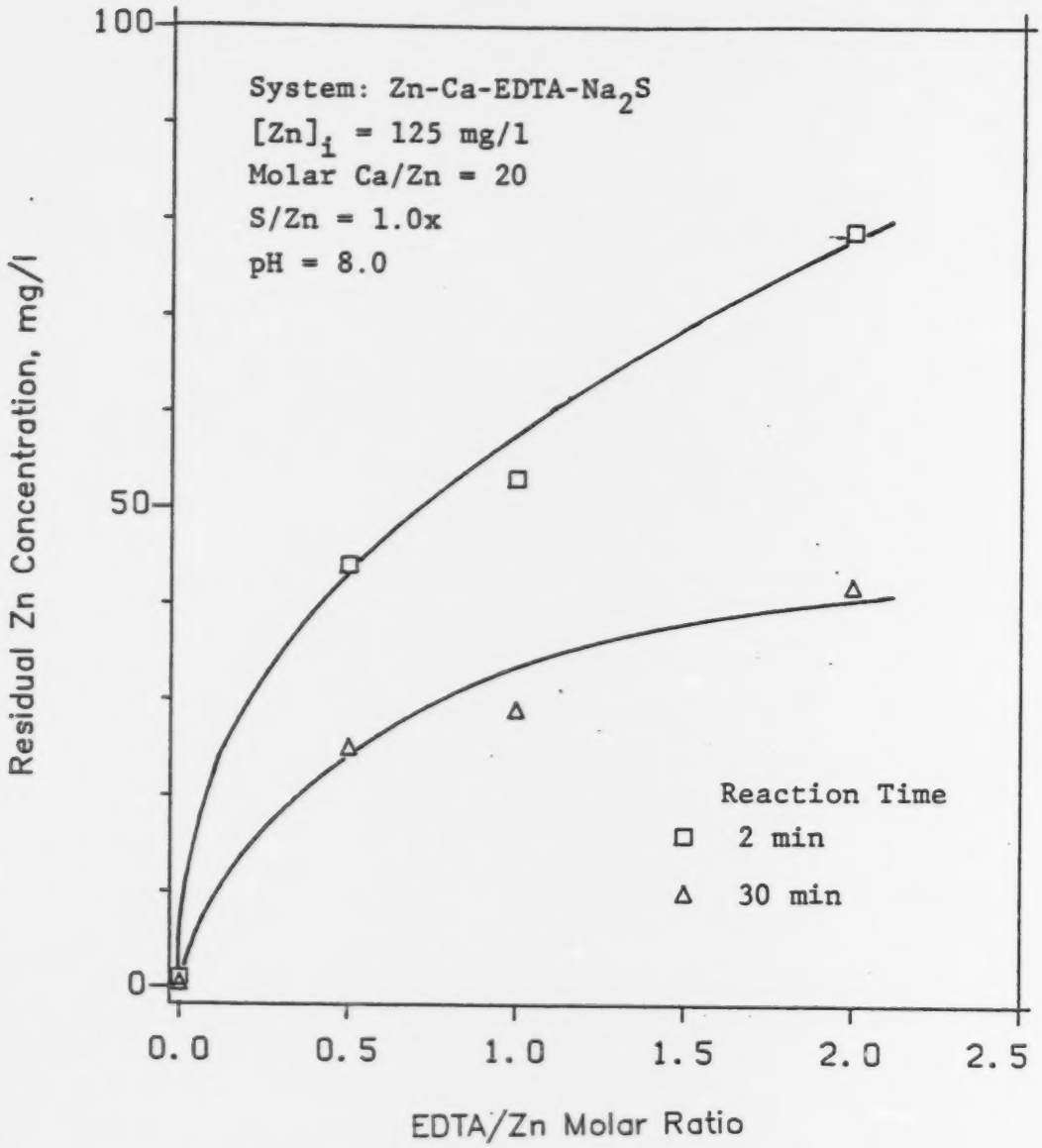

Figure 28. Effect of EDTA/Zn Molar Ratio and Reaction Time on ZnS Precipitation in Zn-Ca-EDTA System.

zinc sulfide precipitation in the presence of large amounts of calcium (at molar Ca/EDTA=20). These experiments were conducted at a stoichiometric sulfide dosage and at pH 8.0. From Figure 28, it can be seen that the residual zinc concentration increased with the EDTA/Zn molar ratio. Figure 28 also shows that at a higher EDTA/Zn molar ratio run, a longer reaction time was needed to reduce the zinc concentration.

Effect of sulfide dosage

All of the previous studies of the Zn-Ca-EDTA-Na_2S system were conducted with the stoichiometric sulfide dosage for zinc. The residual zinc concentration obtained at a reaction time of 30 minutes was 28.5 mg/l for a Ca/EDTA molar ratio of 20 and a EDTA/Zn molar ratio of one. This residual zinc concentration is still too high to meet the effluent standards. It is very likely that the presence of EDTA or calcium reduced the amount of sulfide available to react with zinc. Thus, an experiment was conducted at S/Zn=3.0x and compared with the case with S/Zn=1.0x, the results are shown in Figure 29. It can be seen that increasing the sulfide dosage to S/Zn=3.0x brought the zinc concentration sharply down to below 0.2 mg/l.

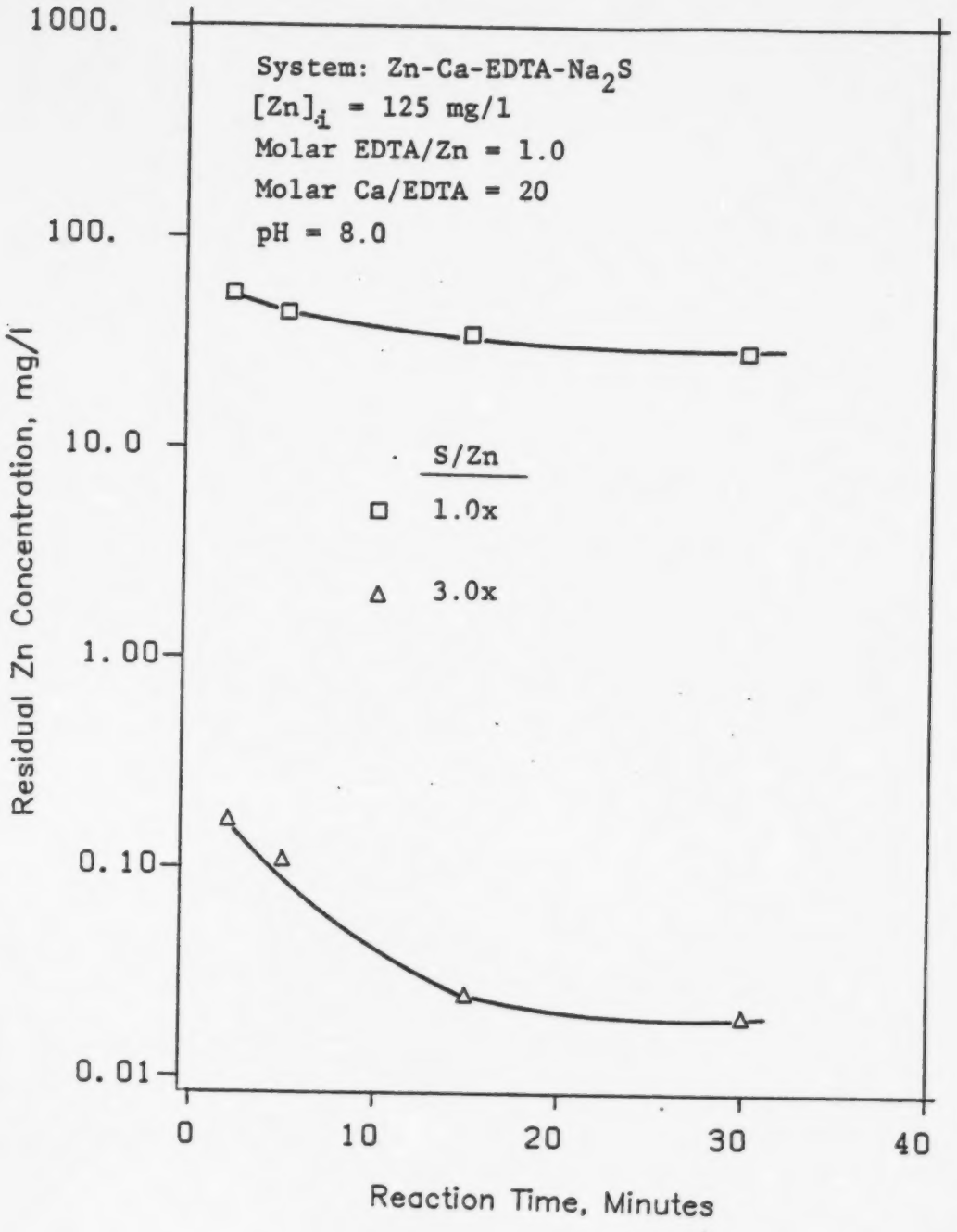

Figure 29 Effect of S/Zn Molar Ratio on ZnS Precipitation in Zn-Ca-EDTA System

FLOCCULATION AND SEDIMENTATION OF METAL SULFIDE PRECIPITATES

It is well-known that metals can be removed effectively by sulfide precipitation because of the low Ksp of metal sulfides. However, the formation of fine particle precipitates in sulfide precipitation processes causes some separation difficulties. Hence, synthetic polymers have been considered for use in the sulfide precipitation processes as flocculants to aggregate the fine particles. Also, some chemicals, such as Al(III), form small polymeric hydroxo-metal complexes in solution. These complexes act as coagulants by absorbing the colloidal particles and neutralizing the charge on the particles.

Cd-Na_2S-Polymer System

Effect of polymer

A polymer, as dissolved in solution, will present different charges on its ionizable groups. In accordance with the charge, polymers are termed anionic, cationic and non-ionic. In order to evaluate the effectiveness of adding polymer as a flocculant, a series of experiments was conducted by adding polymer after the cadmium sulfide precipitation reaction at pH 8.0.

Figure 30 presents the results of experiments for which all three types of polymers were tested in order to decide optimum type and dosage. It shows that the anionic polymer of concentration at 1 mg/l was most efficient for cadmium sulfide precipitate flocculation. This may be due to the fact that most of the precipitates formed in this system are positively charged. Hence, the anionic polymer also acted as a charge neutralizer, the overdosage of anionic polymer ([polymer] > 1 mg/l) resulted in an increase in the supernatant cadmium concentration. This phenomenon can be explained by the restabilization of precipitates.

Effect of pH

At 1 mg/l anionic polymer concentration, a series of experiments was conducted to examine the pH effects on the settling characteristics of cadmium sulfide precipitate. Figure 31 shows the results in terms of supernatant cadmium concentration versus sampling time for various pH values. The supernatant cadmium concentration is lowest under acidic conditions, as shown by the pH 4 results. Since the precipitate particles were surrounded by the hydrogen ion in a low pH range, the use of anionic polymer would be most effective in coagulating the particles in this pH range.

At pH 6.0, results of experiments without polymer are also given in Figure 31 for comparison. It is clear that

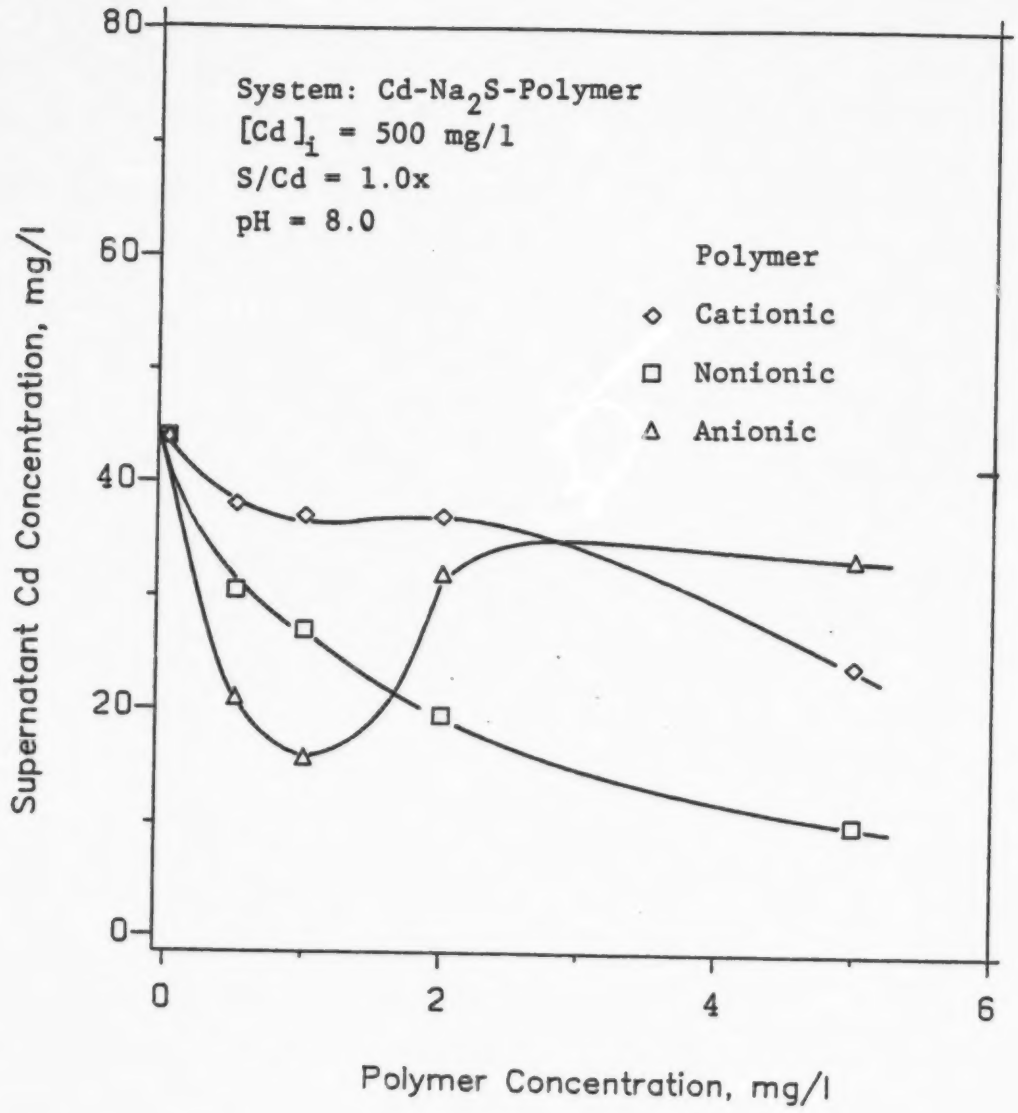

Figure 30. Effect of Polymer Concentration on CdS Precipitate Settling Characteristics by Using Different Types of Polymers.

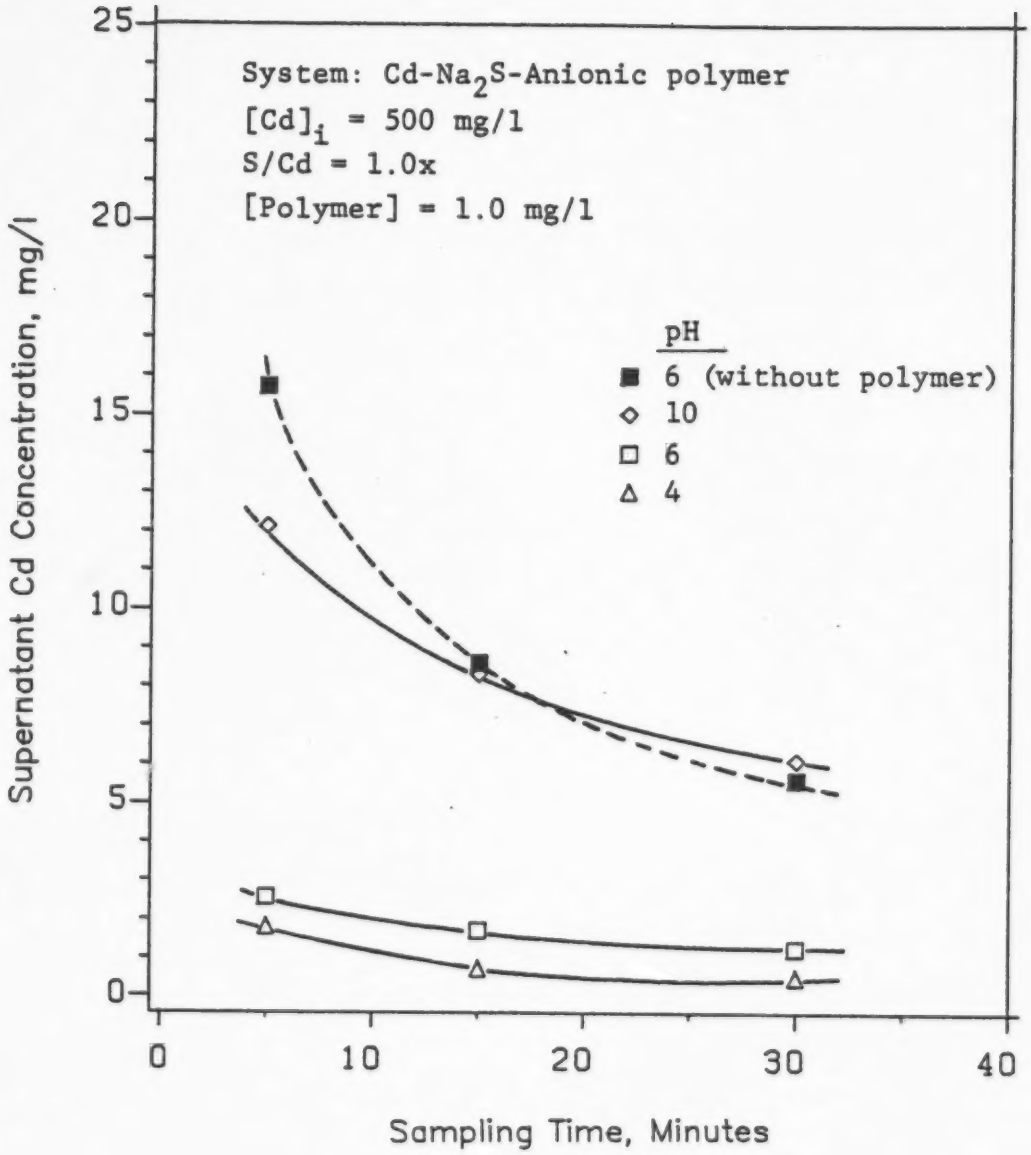

Figure 31. Effect of pH on CdS Precipitate Settling Characteristics in the Presence of Anionic Polymers.

the addition of polymer has pronounced effects. For example, after a settling time of 30 minutes, the addition of polymer at pH 6.0 resulted in a decrease of supernatant cadmium concentration from 5.6 to 1.2 mg/l.

The influence of pH on settling velocity is shown in Figure 32 for the case of 1 mg/l addition of anionic polymer after sulfide precipitation. It indicates that the settling velocity is also a function of pH in the presence of polymer. A higher settling velocity was obtained at lower pH, which also corresponds to low residual cadmium concentration. With the 500 mg/l initial cadmium concentration runs, for example, the settling velocity obtained at pH 4.0 was almost two times higher than that obtained at pH 10.0.

Cd-Ca-Na_2S and Cd-CaS Slurry System

Calcium ion is well-known for its ability to destabilize colloidal particles. In these studies, calcium was used in the cadmium sulfide precipitation system in three different ways: (A) addition of sodium sulfide solution to Cd-Ca mixture, i.e. Cd-Ca-Na_2S system; (B) addition of fresh calcium sulfide slurry, prepared by mixing calcium chloride and sodium sulfide solution, to a cadmium solution; (C) addition of sulfide slurry prepared by using commercial calcium sulfide reagent. The experimental runs were carried out with

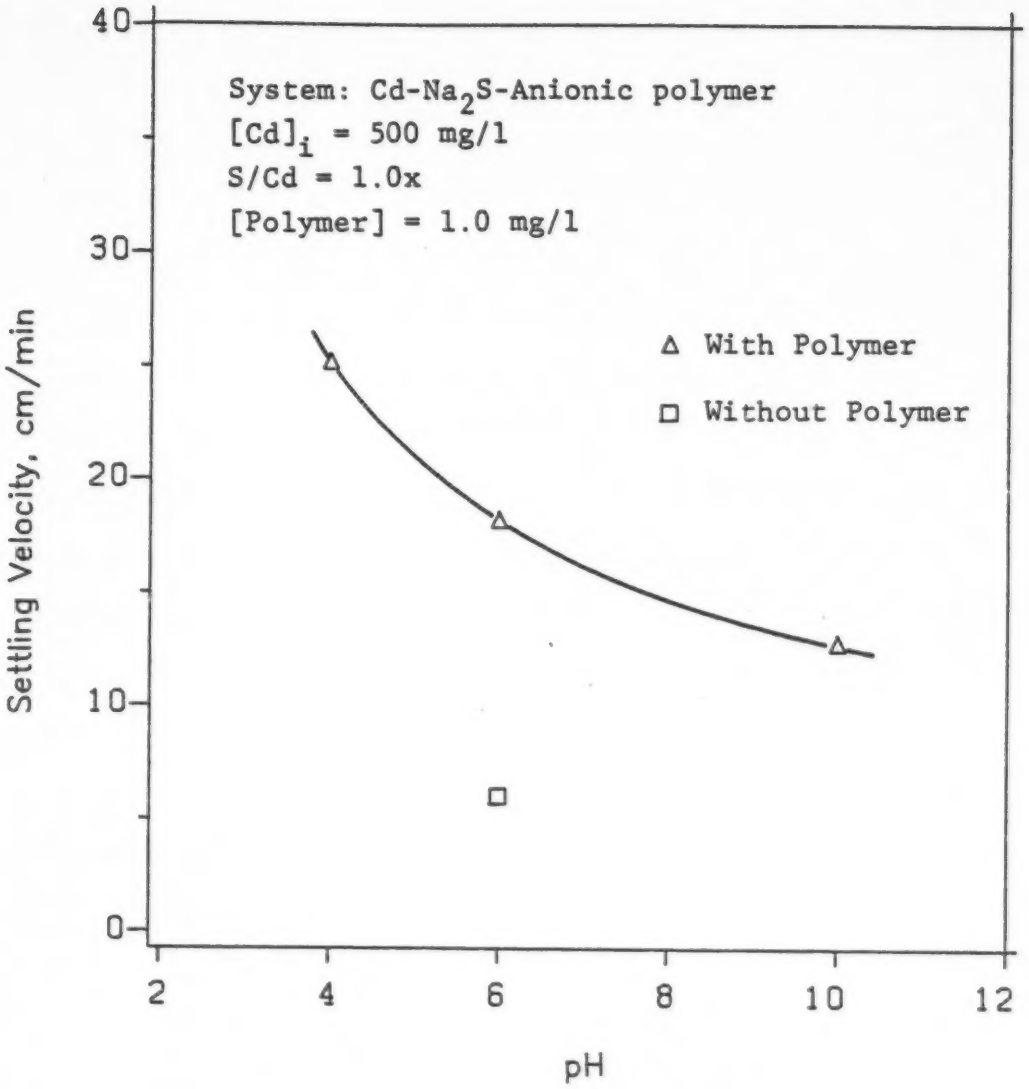

Figure 32. Effect of pH on the Settling Velocity of CdS Precipitate Settling Characteristics in the Presence of Anionic Polymers.

calcium and sulfide dosages which were 1.1x stoichiometric to cadmium. Since the precipitation and coagulation were combined in one step for the above systems, results compared with the no calcium case are also shown in Table 5 for both filtered residual and supernatant cadmium concentration.

The comparison of the residual cadmium concentration in runs B and C shows that the extent of precipitation for Cd-CaS slurry systems corresponds to the calcium sulfide dissolution rate; i.e. the residual cadmium concentration was 6.5 mg/l by using freshly prepared calcium sulfide slurry compared to 265 mg/l by using calcium sulfide slurry prepared from commercial calcium sulfide reagent. For Cd-Ca-Na_2S system, the filtered residual cadmium concentration was the same as that of the Cd-Na_2S system. It again indicated that the presence of calcium has no effect on the extent of precipitation. The resulting supernatant cadmium concentrations indicate that the presence of calcium in both Cd-Ca-Na_2S and Cd-CaS slurry (fresh) systems improved the settling characteristics of cadmium sulfide precipitate significantly.

Additional experiments were conducted at low pH (pH 3.0) for Cd-CaS slurry systems where the slurry was prepared from the commercial calcium sulfide reagent to examine the pH effects. Results are shown in Table 6. In comparison with the results of the pH 8 run (Table 5), the extent of precipitation is significantly improved at low

TABLE 5

Comparison of CdS Precipitation and Settling Characteristics in Different Reaction Systems

Run	System
A	Cd-Ca-Na_2S
B	Cd-CaS Slurry (fresh)
C	Cd-CaS Slurry (commerical)
D	Cd-Na_2S

$[Cd]_i$ = 500 mg/l
S/Cd = 1.1x
pH = 8.0
Reaction time = 30 min
Settling time = 30 min

	Cd Concentration, mg/l	
Run	Filtered Residual	Supernatant
A	< 0.03	11
B	6.5	10
C	265.0	290
D	< 0.03	410

TABLE 6

Comparison of CdS Precipitation and Settling Characteristics by Using Commerical CaS Reagent at pH 3.0

System: Cd-CaS (commerical)
$[Cd]_i$ = 500 mg/l
S/Cd = 1.1x
pH = 3.0
Reaction time = 30 min
Settling time = 30 min

	Cd Concentration, mg/l		
System	Filtered Residual	Supernatant	Settling Velocity, cm/min
CaS (slurry)	< 0.01	20	3.5
CaS (powder)	11.0	41	3.6

pH. For example, the extent of precipitation was only 47% at pH 8.0, and it was almost 100% at pH 3.0. However, the supernatant cadmium concentration obtained with a commercial calcium sulfide reagent at pH 3.0 still indicated poorer settling characteristics of cadmium sulfide precipitate than either Cd-Ca-Na_2S or Cd-CaS slurry (fresh) system.

The results of experiments conducted by adding 1.1x stoichiometric amount of commercial calcium sulfide reagent (powder) directly into cadmium solution are also shown in Table 6 for pH 3.0. No improvement in either the extent of precipitation or the settling characteristics of cadmium sulfide precipitate was shown by this treatment.

SECTION 7

SUMMARY AND CONCLUSIONS

Extensive studies of sulfide precipitation were conducted to remove heavy metals, such as Co, Cd, Cu, Ni, and Zn from synthetic wastewaters. Kinetic studies of nickel and cobalt were conducted in different reactor systems (closed or open). In addition, the interactions between different metals were also investigated for various mixed metal solution systems. In the presence of EDTA, a strong chelating agent, the effectiveness of selective precipitation was evaluated by varying the EDTA concentration and pH. Selective coagulation studies were also conducted with colloidal metal sulfide precipitates by the addition of synthetic polymers. Some metal precipitations were conducted with calcium sulfide slurries (freshly prepared or commercially available) to provide a simultaneous sulfide source and coagulant in one step.

According to the kinetic studies of nickel and cobalt sulfide reaction, the proposed mechanism (equation 33) may be possible for cobalt and nickel reactions; i.e. in the presence of oxygen, dissolution was a consecutive reaction which occurred immediately after sulfide precipitation. The dissolution rate was a function of pH, oxygen, and initial metal concentration. At a lower pH range, the

dissolution rate increased as the pH decreased. With nickel, for example, the soluble nickel was 131 mg/l at pH 6.0, and was 85 mg/l at pH 8.0 at a reaction time of 30 minutes.

At a higher pH range (pH > 10), the dissolution of nickel sulfide was insignificant. At pH 10.0, the soluble nickel was 0.06 mg/l at a reaction time of 30 minutes. As compared with the open reactor case, the dissolution of metal sulfide in a closed reactor was insignificant for nickel and was rather slow for cobalt. Thus, the dissolution may be enhanced in the presence of oxygen. With a higher initial nickel concentration, the dissolution rate was much slower as compared with the lower initial concentration case. For example, with an initial concentration of 50 mg/l, the extent of precipitation increased from zero to a maximum of 80% within 2 minutes and decreased to 18% at a reaction time of 30 minutes; but, with an initial concentration of 5000 mg/l, it increased to a maximum of 98% within 2 minutes, and decreased to 95% at 30 minutes and to 94% for 24 hour runs. Hence, several techniques can be considered to obtain a high degree of removal of nickel or cobalt. For example, effective sulfide precipitation would require operation at a high pH (pH > 10), or in a closed reactor, or with a short detention time.

Effects of the interaction between different metals on sulfide precipitation behavior are summarized. The

results of copper sulfide precipitation in the mixed metal systems, such as Cu-Ni, Cu-Cd-Zn, and Cu-Cd-Ni-Zn, were substantially better compared with the single copper case. In the single copper solution system, the residual copper concentration was reported at 40-50 mg/l if a 0.45 μm filter was used. But for all the copper containing mixed metal solutions being studied, the residual copper concentrations were below 0.02 mg/l (with 0.45 μm filter). It is highly possible that the formation of coprecipitates or coagulation effects are significant in mixed metal systems.

With cadmium, the precipitation behavior was affected mainly in the presence of nickel (Figure 33). In nickel containing systems, such as the Cd-Cu-Ni-Zn-Na_2S system, the residual cadmium concentration increased with time. For the mixed metal system without nickel (such as, the Cd-Cu-Zn-Na_2S system), the residual cadmium concentration obtained was similar (at < 0.03 mg/l) to that of a single cadmium solution system. Therefore, the interaction effects due to copper or zinc are insignificant on the cadmium sulfide precipitation.

With the nickel case, the comparison between various nickel containing mixed metal systems and single nickel systems is shown in Figure 34. Since nickel sulfide dissolution was a function of initial concentration, the comparison should be made with the same level of initial nickel concentration. For the Ni-Zn-Na_2S system, the

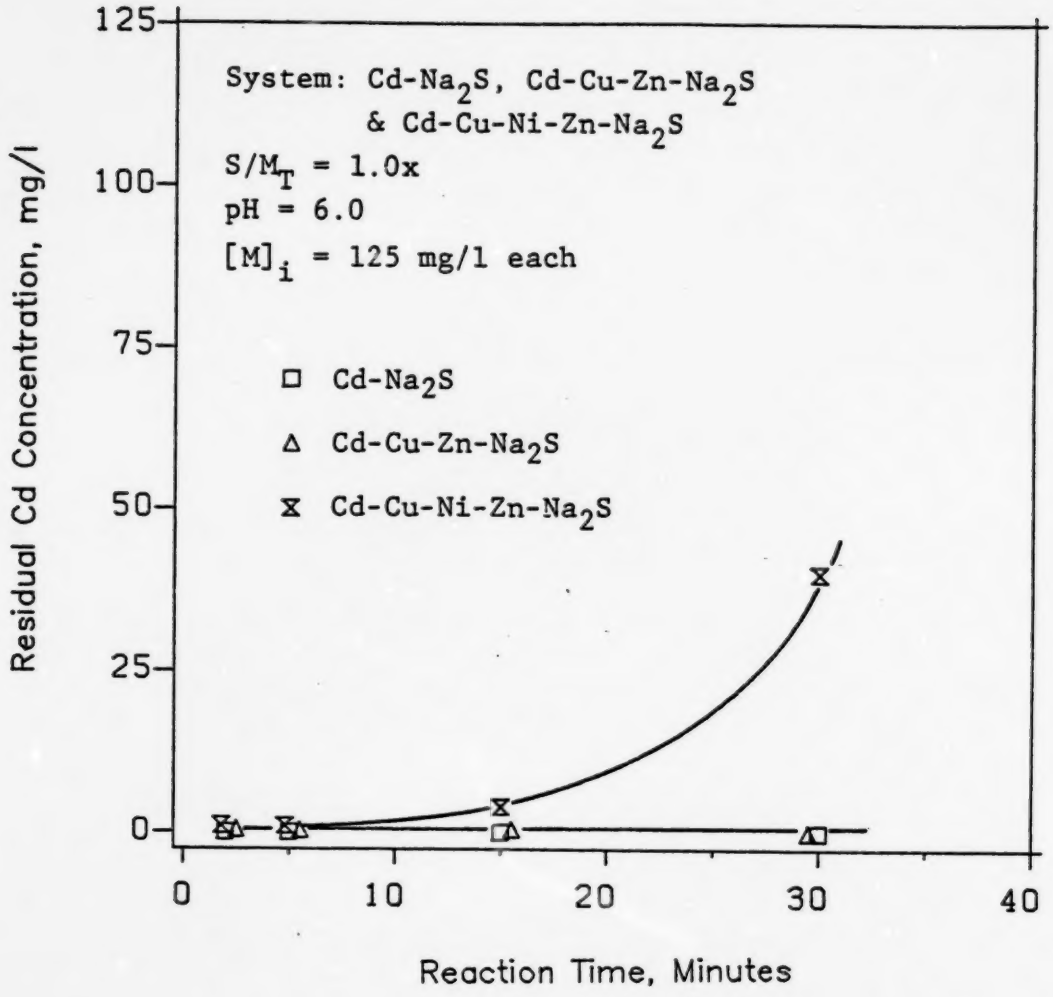

Figure 33. Comparison of Cadmium Precipitation Behavior in Various Metal Sulfide Systems.

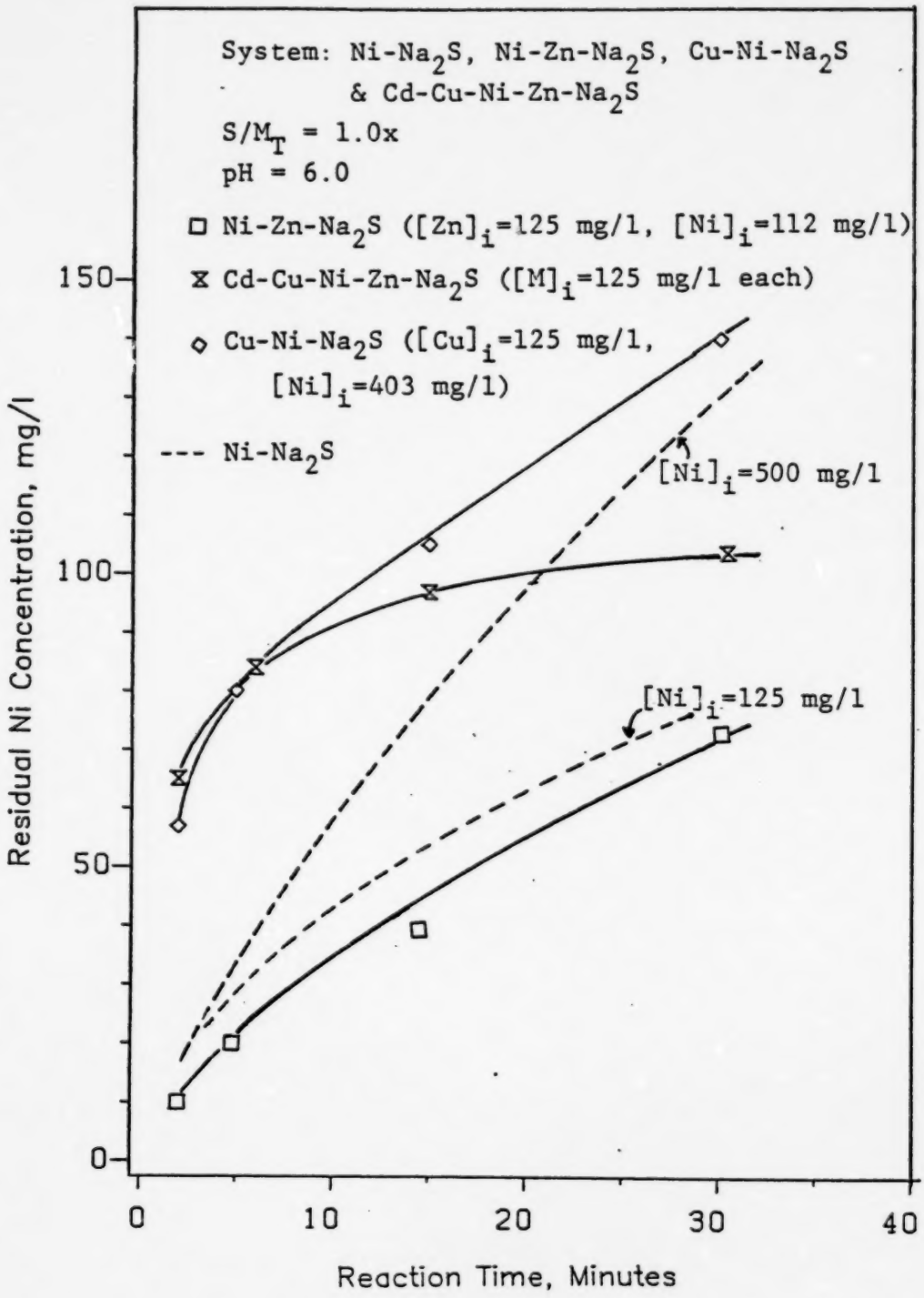

Figure 34. Comparison of Nickel Precipitation Behavior in Various Metal Sulfide Systems.

results were similar to those of single nickel systems with the same initial concentration ($[Ni]_i$=112 mg/l). It is clear that the presence of zinc had no significant effect on the nickel precipitation behavior. Previous studies (12) mentioned the presence of cadmium had no influence on the nickel sulfide precipitation. However, in the Cu-Ni-Na_2S or Cd-Cu-Ni-Zn-Na_2S system, the dissolution rate of nickel sulfide was much higher than for the single nickel solution system with the same initial metal concentration. It indicates that the presence of copper had catalytic effects on the nickel sulfide dissolution.

For zinc, the results of mixed metal solution systems and single metal system are shown in Figure 35. In the mixed metal system without nickel (Cd-Cu-Zn-Na_2S system), the precipitation behavior of zinc was similar to that in single zinc solution system; i.e. the residual zinc concentrations were lower than 0.2 mg/l for both systems with a reaction time of 30 minutes. For Ni-Zn-Na_2S system, the dissolution of zinc sulfide was negligible since the residual zinc concentration increased only from 0.2 mg/l at 2 minutes to 0.5 mg/l at 30 minutes (Figure 15(b)). Thus, the effects of nickel on the zinc precipitation were insignificant in Ni-Zn-Na_2S systems. In the Cd-Cu-Ni-Zn-Na_2S system, the residual zinc concentration increased sharply with time. This may be explained by the fact that copper had catalytic effects on

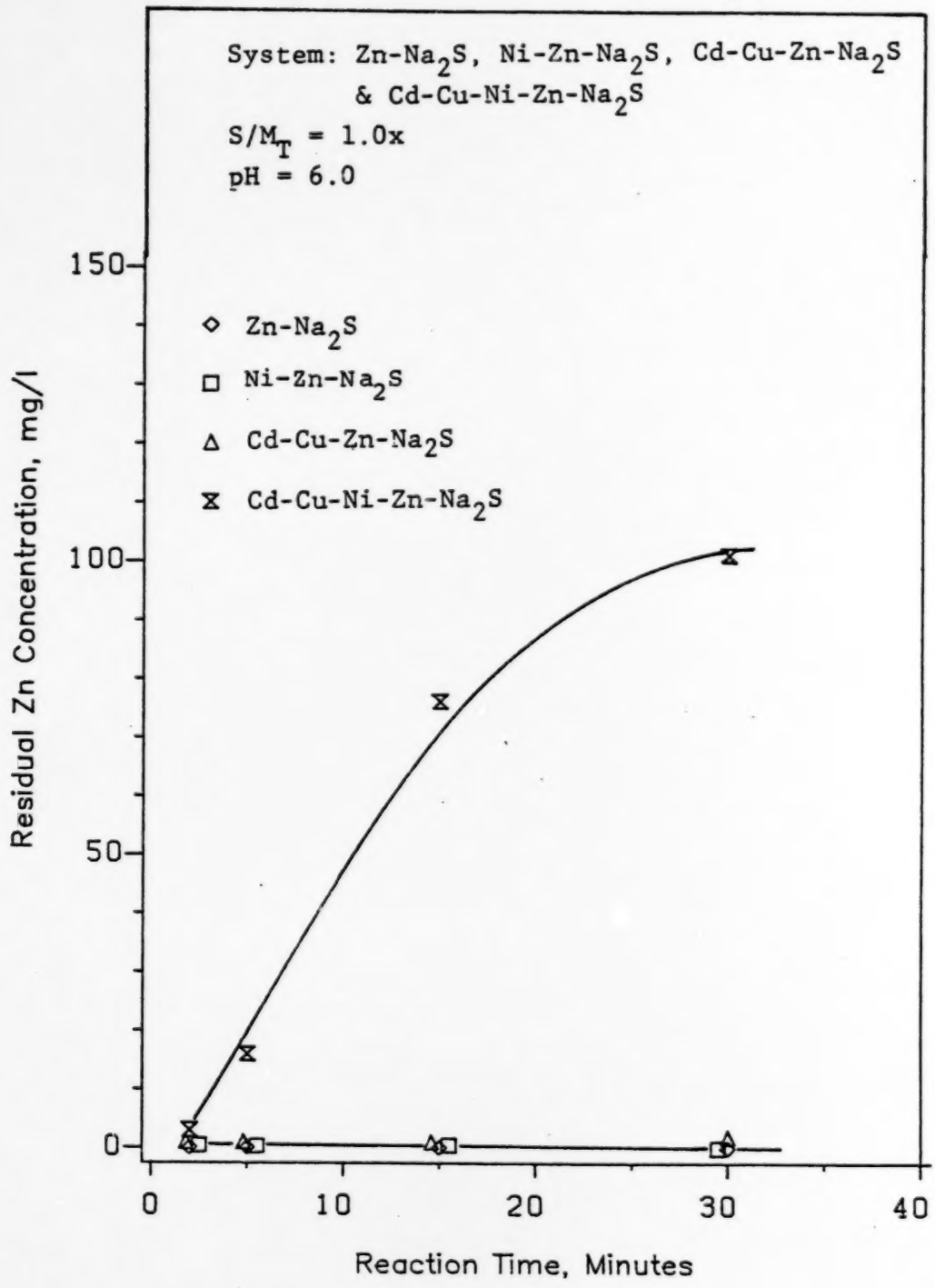

Figure 35. Comparison of Zinc Precipitation Behavior in Various Metal Sulfide Systems.

nickel sulfide dissolution, and thus resulted in the dissolution of zinc sulfide.

Because of the interaction effects, the multi-metal precipitations conducted with S/M_T=1.0x and at pH 6.0 were not complete except for copper. The addition of a higher sulfide dosage (S/M_T > 1.0x) was effective in bringing down the residual cadmium concentration to 7 mg/l at S/M_T=1.5x, but it was not effective for zinc or nickel. In order to remove all the metals in one step, a high pH value was required. At pH 10.0, for example, all the residual concentrations of the metals in Cd-Cu-Ni-Zn-Na_2S system were reduced to a level lower than 0.08 mg/l.

In the presence of EDTA, the extent of metal sulfide precipitation was reduced corresponding to the increase of the apparent stability constant (K'_{ML}, as a function of pH) of M-EDTA complexes and the amount of EDTA. For example, in a Cd-EDTA-Na_2S system with molar EDTA/Cd=1.0, the residual cadmium concentration was < 10 mg/l at pH < 4 where the apparent stability constant was low, and it was > 110 mg/l at pH > 8 where the apparent stability constant was high (Figure 22). With a low EDTA concentration (molar EDTA/Cd < 0.5), the EDTA effects were negligible and a high degree of precipitation could be obtained (Figure 23). For the purpose of selective precipitation, the addition of a proper amount of EDTA and adjustment of pH was found to be an effective technique.

In Ni-Zn-EDTA-Na_2S system, for example, the presence of EDTA (at molar EDTA/Ni=1.0) resulted in the selective metal separation where zinc was removed and nickel remained soluble (94% zinc removal and 10% nickel removal) at a short reaction time (Figure 24). In addition, the separation extent in a closed reactor was the same as in an open reactor in the presence of the same amount of EDTA. To obtain a high degree of removal of metals (in the presence of EDTA), the addition of calcium was effective to reduce the EDTA effects and to increase the extent of precipitation. For example, the addition of calcium at molar Ca/EDTA=20 substantially decreased the residual zinc concentration to 28.5 mg/l from 56.5 mg/l where no calcium was added with a reaction time of 30 minutes (Figure 27).

Precipitation was significantly improved with the addition of a high sulfide dosage when calcium was added to the EDTA containing systems. In Ni-Ca-EDTA-Na_2S systems, for example, the residual zinc concentration decreased to 0.02 mg/l at S/Zn=3.0x from 28.5 mg/l at S/Zn=1.0x (Figure 29).

Some experiments were conducted to understand the formation of colloidal precipitates. In general, the particle size of precipitates corresponds to Ksp values. For most metal sulfides the Ksp values are very low, thus the precipitates were colloidal or fine particles because of the high decree of supersaturation.

The pH value was also found to have significant effects on the particle size. In the studies of cadmium sulfide precipitation, the higher pH values (pH > 8) favored the formation of some colloidal precipitates. The use of an ultrafiltration membrane (with 10,000 MW cut-off) to refilter the filtrate obtained by using 0.45 μm filter, showed that the residual cadmium concentration could be reduced from 1.3 to 0.01 mg/l at pH 10.0. Thus, the high residual concentration at high pH, which disagreed with the theoretical solubility curve, was contributed by the presence of colloidal particles.

Since the formation of colloidal precipitates causes problems in filtration or settling processes, coagulants, such as synthetic polymers and calcium ion, were added to coagulate the colloidal precipitates. The effectiveness of synthetic polymers was controlled by the type of polymer, polymer concentration and pH. Among three types of polymers (cationic, anionic and non-ionic polymer), anionic polymer was most efficient to reduce the supernatant metal concentration. For example, the addition of 1 mg/l of anionic polymer dropped the supernatant cadmium concentration (with 30 minute settling) to 16 mg/l from 44 mg/l when no polymer was added (Figure 30).

Using the anionic polymer at a concentration of 1 mg/l, it was shown that pH had significant effects on the settling characteristics of the precipitate. As the pH

decreased, the supernatant metal concentration decreased and the settling velocity increased. With the cadmium sulfide precipitate, for example, the supernatant concentration (with 30 minute settling) was 6.1 mg/l and the settling velocity was 12.8 cm/min at pH 10.0; but the supernatant concentration was 0.5 mg/l and the settling velocity was 25.2 cm/min at pH 4.0.

In order to add calcium effectively into the system as a coagulant, various addition techniques were conducted, such as, adding calcium before sulfide precipitation, using freshly prepared calcium sulfide slurry, or using commercially available calcium sulfide reagent. Although the dissolution of calcium sulfide affected the extent of precipitation, the resulting supernatant concentrations indicate that the presence of calcium significantly improved the settling characteristics of the cadmium sulfide precipitate. For example, the supernatant cadmium concentration (with 30 minute settling) was 410 mg/l in the absence of calcium, and it was 11, 10 and 290 mg/l for Cd-Ca-Na_2S, Cd-CaS slurry (freshly prepared), and Cd-CaS slurry (commercially available), respectively.

The important conclusions are:

- Metal interactions had significant effects on the precipitation behavior of cadmium, zinc, or nickel mainly because the nickel ion had catalytic effects on nickel sulfide oxidation.

- Selective precipitation can be achieved effectively in the presence of the proper amount of EDTA and the adjustment of pH.
- High pH (pH > 8) favored the formation of some colloidal cadmium sulfide precipitate.
- The settling characteristics of precipitates could be significantly improved with the addition of anionic polymer at a lower pH or the use of freshly prepared calcium sulfide slurry.
- In the presence of EDTA, a high degree of metal removal with sulfide could be achieved with the addition of calcium.

Further recommended studies are:

1. More kinetic studies for cobalt and nickel reaction with sulfide to obtain the possible reaction rate expression.
2. Identification of soluble sulfur species formed during NiS and CoS dissolution.
3. Further studies of the catalytic effects of nickel and copper on metal dissolution.
4. Design for continuous separation, flocculation, settling, and filtration on the basis of the data obtained in this study.
5. Search for some inhibitors to prevent the dissolution of nickel sulfide and cobalt sulfide in the presence of oxygen.

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